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Systech Corp., Xenia, OH

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This report presents the results of testing, sampling and analysis of three resource recovery facilities burning municipal wastes for emissions of tetra chlorinated dioxins and furans in the flue gas. The stack emissions were analyzed by the EPA PTMAX dispersion model to determine maximum 1-hour ground level concentrations, which were found to range from 10^{-13} g/m^3 to 10^{-12} g/m^3. A wide distribution of isomers were reported both for TCDDs and TCDFs. The most toxic 2378 TCDD isomer emissions from the stack ranged from 3.4 to 180 mg per ton of the fuel fired, while 2,378 TCDFs ranged from 22 to 1800 ug/ton.

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AN EVALUATION OF TRACE ORGANIC EMISSIONS FROM REFUSE THERMAL PROCESSING FACILITIES

By

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FOREWORD

The movement toward resource recovery programs as a means of solid waste disposal has led to the establishment of incineration as a major disposal option. Since the early 1970s, many incinerator facilities utilizing various energy recovery technologies have been designed and placed into operation. While their success at achieving efficient energy recovery has been quite variable, all facilities have had to deal with one common obstacle: controlling the emissions of toxic compounds into the surrounding environment.

This report deals specifically with the problem of tetrachlorodibenzo-p-dioxin (TCDD) and tetrachlorodibenzofuran (TCDF) emissions from incinerator facilities. The test program upon which this report is based was conducted by SYSTECH Corporation, Xenia, Ohio, for the U.S. EPA Office of Solid Waste under Contract No. 68-01-6071.

ABSTRACT

This report presents the results of a test program conducted by SYSTECH Corporation for the United States Environmental Protection Agency Office of Solid Waste (EPA/OSW) to investigate the emissions of tetrachlorodibenzo-p-dioxins (TCDDs) and tetrachlorodibenzofurans (TCDFs) from three different refuse burning resource recovery facilities.

A comprehensive program of sampling, data collection, analysis, and dispersion modelling was performed. Samples collected and analyzed included solid and liquid process streams as well as flue gas samples collected by SASS and Modified Method 5 trains. Analysis was performed employing both packed column and capillary column GC/HRMS.

The major conclusions of this program indicated that the emission rates from three different test facilities for TCDDs and TCDFs ranged from 10^{-9} g/sec to 10^{-7} g/sec and 10^{-8} g/sec to 10^{-6} g/sec, respectively. The emission rates of TCDDs were analyzed by the EPA PTMAX dispersion model to determine maximum 1-hr expected ground level concentrations. The results of this analysis indicated concentrations on the order of 10^{-13} g/m^3 to 10^{-12} g/m^3. The results of packed column and capillary column GC/HRMS analysis showed that packed column analysis provides a useful "worst case" assessment of the amounts of 2,3,7,8 isomers present. Capillary column analyses indicated a wide distribution of isomers reporting for both TCDDs and TCDFs. The analysis of other process samples strongly suggest the need for further study of TCDD and TCDF emissions from municipal refuse combustion facilities.

This report was submitted in fulfillment of Contract No. 68-01-6071, Work Assignment No. 18, by SYSTECH Corporation under the sponsorship of the U.S. EPA/OSW. This report covers the period from April 14, 1981 to March 31, 1982.

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The successful completion of this project required the participation and cooperation of a number of individuals from the private, scientific, and government sectors. We are particularly indebted to the plant managers and personnel at the test facilities; to Dr. Brenda Kimble, Laboratory for Energy Related Health Research, University of California, Davis, California; and to Dr. Michael Gross and his staff at the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, Lincoln, Nebraska. We would also like to thank Mr. Randy Chrismon and Mr. David Sussman, U.S. EPA Office of Solid Waste, for their cooperation and support in successfully completing this project.

SECTION 1

INTRODUCTION

BACKGROUND

The movement toward resource recovery programs as a means of municipal refuse disposal has led to the establishment of combustion with energy recovery as a major disposal option. Since the early 1970's many refuse combustion facilities using various energy recovery technologies have been designed and placed into operation. While all facilities have been challenged by technical and economic problems, in recent years another common obstacle has emerged: controlling the emissions of toxic compounds into the surrounding environment.

Two classes of such compounds which have received considerable recent attention are the tetrachlorodibenzo-p-dioxins (TCDDs) and tetrachlorodibenzofurans (TCDFs). Several reports have described the occurrence of TCDDs and TCDFs in fly ash and flue gases from municipal incinerators and industrial heating facilities.[1,2,3] These reports have been met with great concern, primarily because of the toxicity of specific isomers of these compounds, especially 2,3,7,8-TCDD and 2,3,7,8-TCDF.[4,5] In 1979, the U.S. Environmental Protection Agency (EPA) became involved in an investigation of a municipal incinerator to determine whether TCDDs were being emitted from the facility. Although this study did not provide conclusive evidence regarding the emission of TCDDs, it did motivate an interest within the EPA to pursue more rigorous testing at resource recovery facilities to quantify the emissions of TCDDs and TCDFs.

PROGRAM OBJECTIVE

In 1980, the EPA Office of Solid Waste (OSW) initiated a test program to investigate the emissions of TCDDs and TCDFs from refuse burning resource recovery facilities. This report summarizes the work conducted in this program by SYSTECH Corporation for the OSW under EPA Contract No. 68-01-6071. The primary objective of this program was to determine whether TCDDs and TCDFs are emitted from refuse combustion facilities. If initial data indicated that these compounds were in fact being emitted, a number of further steps would be pursued:

- A subset of the samples would be analyzed to quantify the most toxic isomers of these compounds: 2,3,7,8-TCDD and 2,3,7,8-TCDF.

- The results of the TCDD analyses would be used to predict maximum expected ground level concentrations through the application of computer dispersion modeling techniques.

- A subset of the fuel, ash, and combustion air samples taken during the program would be analyzed to provide supporting information for the emissions results.

In order to accomplish these objectives, a comprehensive program of sampling, data collection, analysis, and dispersion modeling was initiated. It should be noted that the experimental design employed for this program was not intended to precisely quantify, in a statistically rigorous manner, the amounts of TCDDs and TCDFs being emitted from the facilities. Because of the limited resources and time available for this test program, a definitive test was beyond the scope of the present level of effort. The test program as described in this report must therefore be interpreted as a limited characterization of the average concentrations of TCDDs and TCDFs being emitted from the facilities during the sampling periods.

PROGRAM PARTICIPANTS

Because of the complexity of this program, a number of participants were involved in various phases of the evaluations. SYSTECH conducted all field activities and source sampling required for these evaluations according to procedures set forth in the document Test Protocol: An Environmental Assessment of Refuse Thermal Processing Facilities, prepared by SYSTECH under EPA Contract No. 68-01-6071.[6] SYSTECH was assisted in the preparation of this protocol and in the performance of trace organic sampling activities by Dr. Brenda Kimble, Laboratory for Energy Related Health Research, University of California, Davis, California. All sample extractions and analyses for TCDDs and TCDFs were conducted by Dr. Michael Gross, Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, Lincoln, Nebraska. SYSTECH was responsible for the compilation of all test data and for the presentation of this final report.

PROGRAM OUTLINE

During 1980 and 1981, SYSTECH Corporation conducted testing at three facilities burning municipal solid waste (MSW) to determine whether TCDDs and TCDFs were being emitted. These facilities included a small modular incinerator, a field erected refractory wall incinerator, and a stoker fired waterwall boiler. Since the initial agreement to permit testing at these facilities required that they not be referred to by name in any subsequent reporting, they are described in this report as Facilities A, B, and C. A detailed description of the facilities is included in Section 2 of this report. The test programs conducted at these facilities are outlined as follows.

Sampling Program

The emissions at each facility were to be evaluated over 3-day sampling periods designed under the direction of the EPA/OSW to provide a data base similar to that which has historically been used by federal regulatory agencies in establishing regulations and by the air pollution control industry in the design of control devices. Facility A, the small modular incinerator, was evaluated during two 3-day test periods, first while burning refuse preprocessed by trommeling for size separation and then while burning as-received refuse. The field erected heat recovery incinerator, Facility B, was evaluated over one 3-day test period while co-firing refuse and waste oil. Facility C was evaluated during only two 1-day test periods because of system operation problems. During the first period the boiler was operated on densified refuse-derived fuel (dRDF) only, and during the second period only coal was burned.

Tables 1 and 2 summarize the field activities required for this environmental evaluation. These activities have been categorized into those required to document facility performance and those required to characterize the trace organic composition of the various process streams.

Facility Performance Data--

The activities required to document facility performance were directed primarily at characterizing mass flow rates, excess air levels, system temperatures, and particulate emissions. Mass flow rates of fuel and ash were determined by direct measurements as indicated in Table 1. Mass flow rates of flue gases were determined from the stoichiometric air requirements as determined from the fuel ultimate analysis and from the measured excess air levels. System temperatures were determined by monitoring thermocouples set up to record combustion zone and boiler outlet temperatures. Stack temperatures were monitored in conjunction with the stack test runs. Particulate emissions were determined from the performance of Method 5 testing.

Trace Organic Composition Data--

Table 2 summarizes the field activities pursued to characterize the trace organic emissions from the facilities. Sampling was conducted to provide supplementary data on the TCDD and TCDF concentrations of the solid and liquid process streams as indicated in Table 2. The methods employed in these activities are outlined in the SYSTECH Test Protocol.[6]

The major focus of this program was to characterize the stack emissions of TCDDs and TCDFs. This was accomplished by sampling the stack gases as indicated in Table 2 with Modified Method 5 and SASS trains. The SASS train was employed only at Facility A. Detailed procedures for these sampling activities are included in the aforementioned protocol.[6]

Modified Method 5 train--A schematic of the Modified Method 5 train used in this program is shown in Figure 1. The train is designed for the collection of particulates and volatile matter from ducts and stacks. A sample is collected through a glass lined probe and then passed through a

TABLE 1. FIELD ACTIVITIES FOR ENVIRONMENTAL EVALUATION--FACILITY PERFORMANCE DATA

Measurement number	Stream sampled	Measurement required	Sample size	Frequency	Measurement methods
1	Municipal waste	Hourly feed rate	NA	As charged	Load cells, feeder scales, or truck weights
2	Other primary fuels	Hourly feed rate or daily consumption	NA	As charged or hourly	Feeder scales or flow meter
3	Auxiliary fuels	Daily consumption	NA	Hourly	Flow meter
4	Fuel properties	Moisture and	1.5 kg	Daily composite samples split from hourly grabs	Drying oven
		ultimate analysis	1.5 kg	Test period composite samples from daily composites	ASTM D3176
5	Bottom ash	Daily production	NA	As removed	Truck weights
6	Bottom ash	Moisture	1.5 kg	Three daily composite samples	Drying oven
7	Control device ash	Daily production	NA	As removed	Truck weights
8	Boiler outlet	Temperature	NA	Hourly	Thermocouple/temperature recorder

(continued)

TABLE 1. (continued)

Measurement number	Stream sampled	Measurement required	Sample size	Frequency	Measurement methods
9	Boiler outlet	CO_2	NA	Continuous	Nondispersive infrared (NIR) analysis
10	Boiler outlet	O_2	NA	Continuous	Electro-chemical cell
11	"	CO	NA	Continuous	NDIR
12	"	NO_x	NA	Continuous	Electro-chemical cell or EPA M-7
13	"	SO_x	NA	Continuous	Electro-chemical cell or EPA M-6
14	Stack	Temperature	NA	2 per day	Modified Method 5 (MM5) and SASS data
15	"	Moisture	NA	3 runs per test	Method 5 data
16	"	Volume/ velocity	NA	2 per day	Pitot tube traverse
17	"	Particulate emissions	>60 scf* per run	3 runs per test	Method 5
18	Facility	Operating conditions	NA	Hourly	Monitor system control instrumentation

* Standard cubic feet.
NA Not applicable.

TABLE 2. FIELD ACTIVITIES FOR ENVIRONMENTAL EVALUATION— TRACE ORGANIC CHARACTERIZATION DATA

Measurement number	Stream sampled	Measurement required	Sample size	Frequency	Measurement methods
1	Other primary fuels	Trace organics	1 liter	Once	GC/HRMS*
2	Bottom ash	Trace organics	1.5 kg	Three daily composite samples + bulk sample	GC/HRMS
3	Control device ash	Trace organics	1.5 kg	Three daily composite samples + bulk sample	GC/HRMS
4	Stack	Trace organic sampling (MM5)	16 m^3 (8 m^3 per train	1 per day	GC/HRMS
5	"	Trace organic sampling (SASS train)†	30 m^3	1 per day	GC/HRMS
6	Combustion air	Trace organics (resin collection system)	25 m^3	1 per day	GC/HRMS
7	"	Trace organics (Hi-Vol system)	800 m^3	1 per day	GC/HRMS

* Gas chromatography/high resolution mass spectrometry.

† The SASS train was employed for testing only at Facility A.

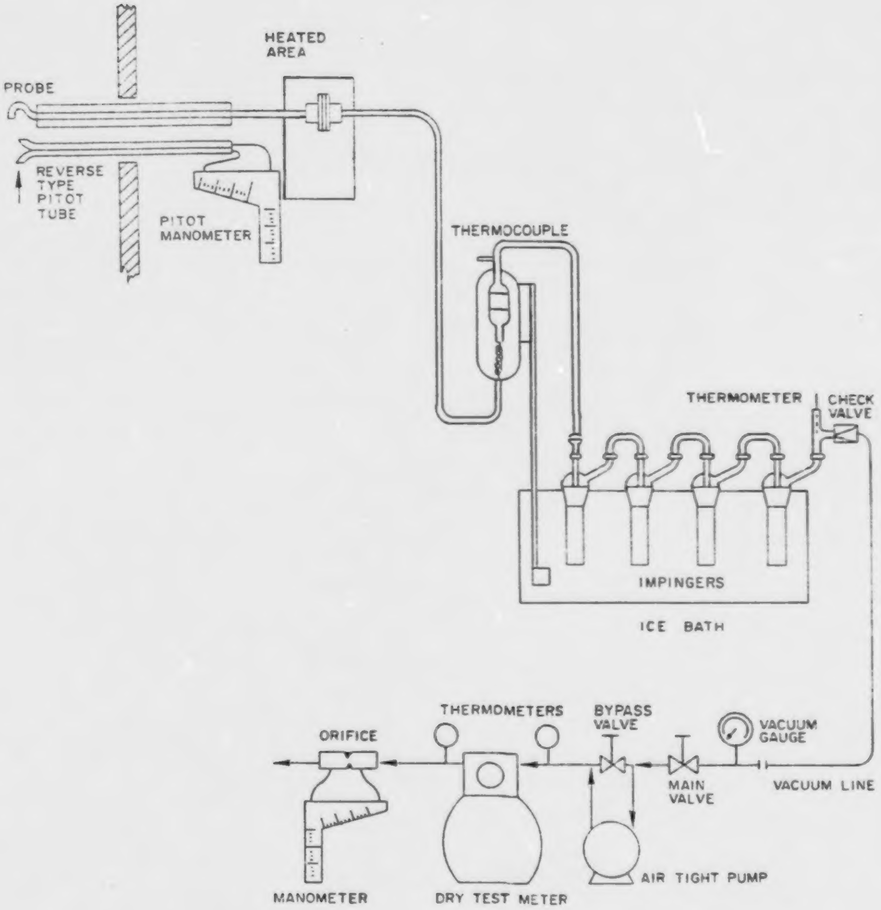
HEATED AREA
PROBE
REVERSE TYPE PITOT TUBE
PITOT MANOMETER
THERMOCOUPLE
THERMOMETER
CHECK VALVE
IMPINGERS
ICE BATH
THERMOMETERS
BYPASS VALVE
VACUUM GAUGE
ORIFICE
MAIN VALVE
VACUUM LINE
AIR TIGHT PUMP
MANOMETER
DRY TEST METER

Figure 1. Modified Method 5 train.

particulate filter (Reeve Angel 934AH), both heated to 121°C. Vaporous material conducted through the filter is carried by Teflon tubing to a water cooled XAD-2 sorbent resin trap. This trap is illustrated in Figure 2. Cold water from the impinger ice bath is pumped through the jacket of the trap to maintain a gas outlet temperature below 20°C. Gas exiting from the resin trap is conducted by Teflon tubing into a bank of four ice cooled impingers. The first impinger in the train contains 100 mℓ of glass distilled HPLC grade water for condensate trapping, the second and third are condensate overflow reservoirs, and the final impinger contains ~500 grams of silica gel to prevent the entry of moisture into the pump.

Identical Modified Method 5 sample trains were operated simultaneously on the stack at each facility to provide combined daily sample volumes of approximately 16 m^3 (565 scf). The trains were leak checked before and after each testing period according to the Code of Federal Regulations 40 CFR 60 Appendix A, Reference Methods. Because the trains sampled at a rate of approximately 28 ℓ/min (1 cfm), a 5-hr sampling program was required to obtain the 16-m^3 sample. This factor, together with the logistical difficulties of duplicate simultaneous sampling of the same stack, necessitated a deviation from commonly employed traverse procedures. The sampling program was conducted by placing the two probes at 90° angles in two of the stack access ports and traversing each across the stack diameter. This was accomplished by completely inserting one probe and inserting the other probe just inside the stack at the beginning of the test run. The probes were then traversed until their respective penetrations were exchanged at the end of 5 hours. Standard 40 CFR 60 Method 5 procedures were followed as closely as possible in all respects.

SASS* train--The SASS train used in this program is shown schematically in Figure 3. The SASS is an integrated sampling system designed specifically for the collection of particulates and volatile matter from ducts and stacks. It contains components for the separate collection of particulates and vaporous trace organics. Particulates are collected by a bank of three cyclones and a backup filter all maintained at a constant 205°C. This temperature control ensures that condensation of water vapors does not occur in this section of the train and that size separation cut points are reproducibly defined. The cyclones partition the particulate matter into three nominal size ranges defined by mean particle diameter: >10 μm, 10-3 μm, and 3-1 μm. The filter catch represents particles <1 μm in size that are retained on a standard Gelman Type AE 142-mm × 0.016-in glass fiber filter.

Vaporous materials and ultrafine particles not collected by the particulate sampling component of the train are cooled to 20°C and passed through a porous polymer resin bed of XAD-2 sorbent (see Figure 4). Condensate formed in the cooling process is also passed through the XAD-2 and collected in a reservoir.

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* Manufactured by the Acurex Corporation/Aerotherm Group, 485 Clyde Ave., Mountain View, California, 94042, (415) 964-3200.

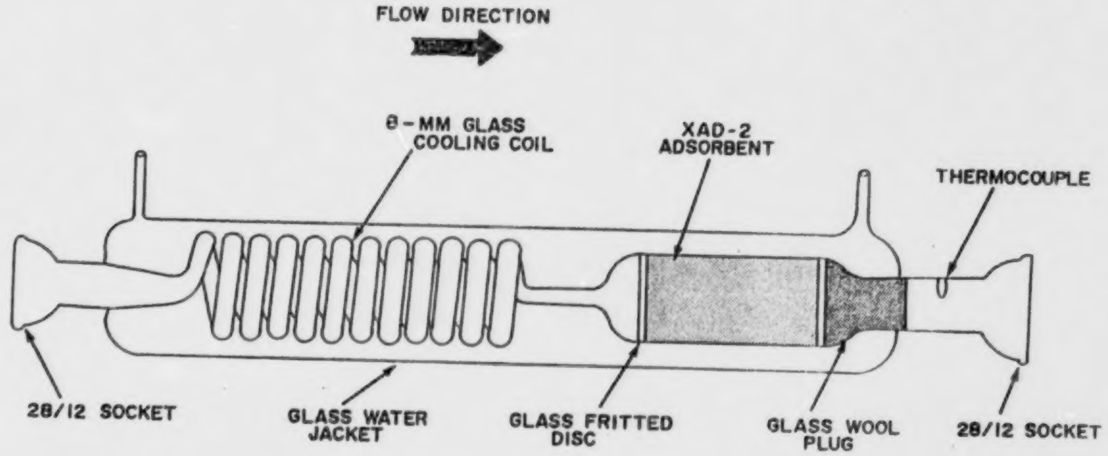
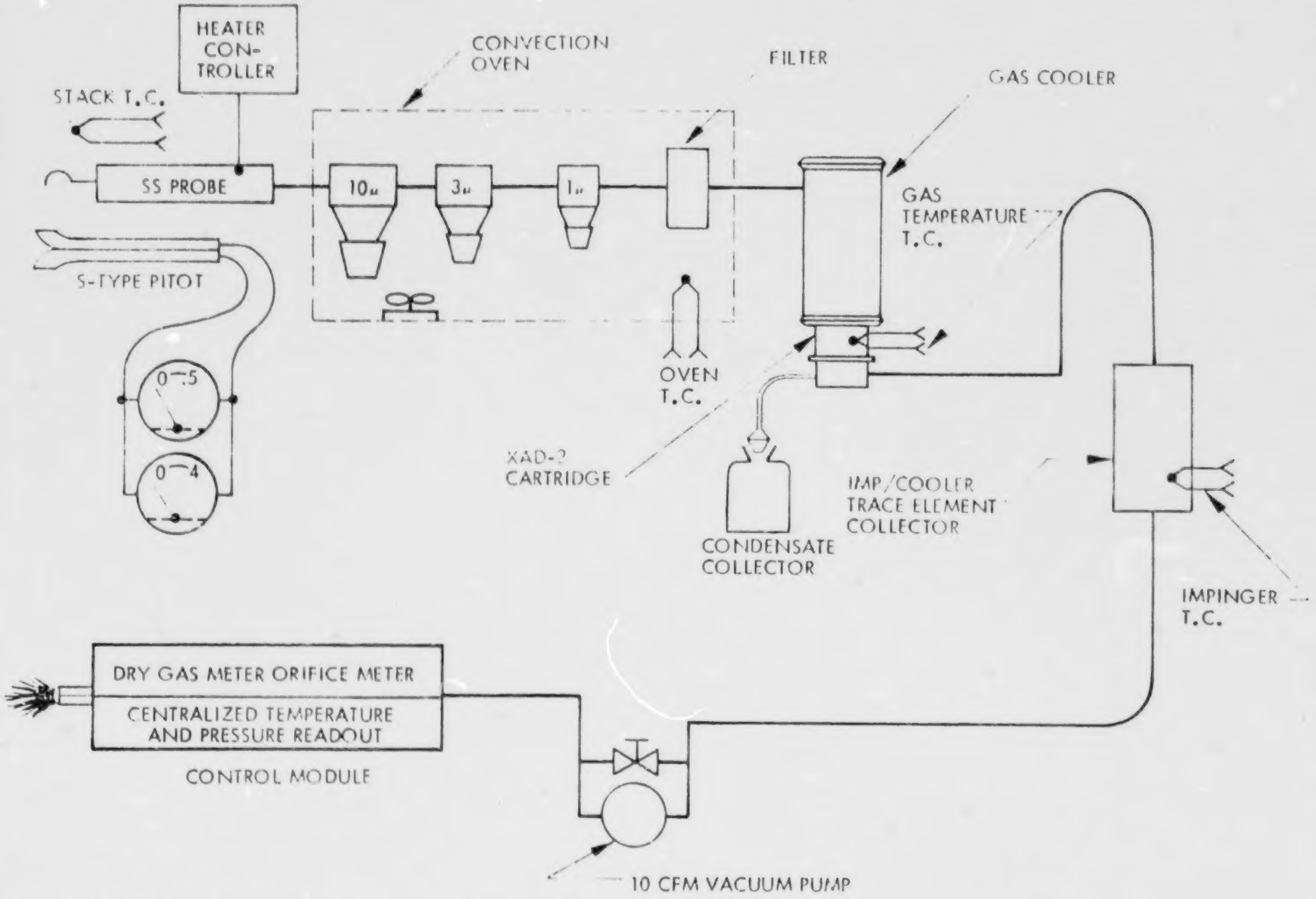
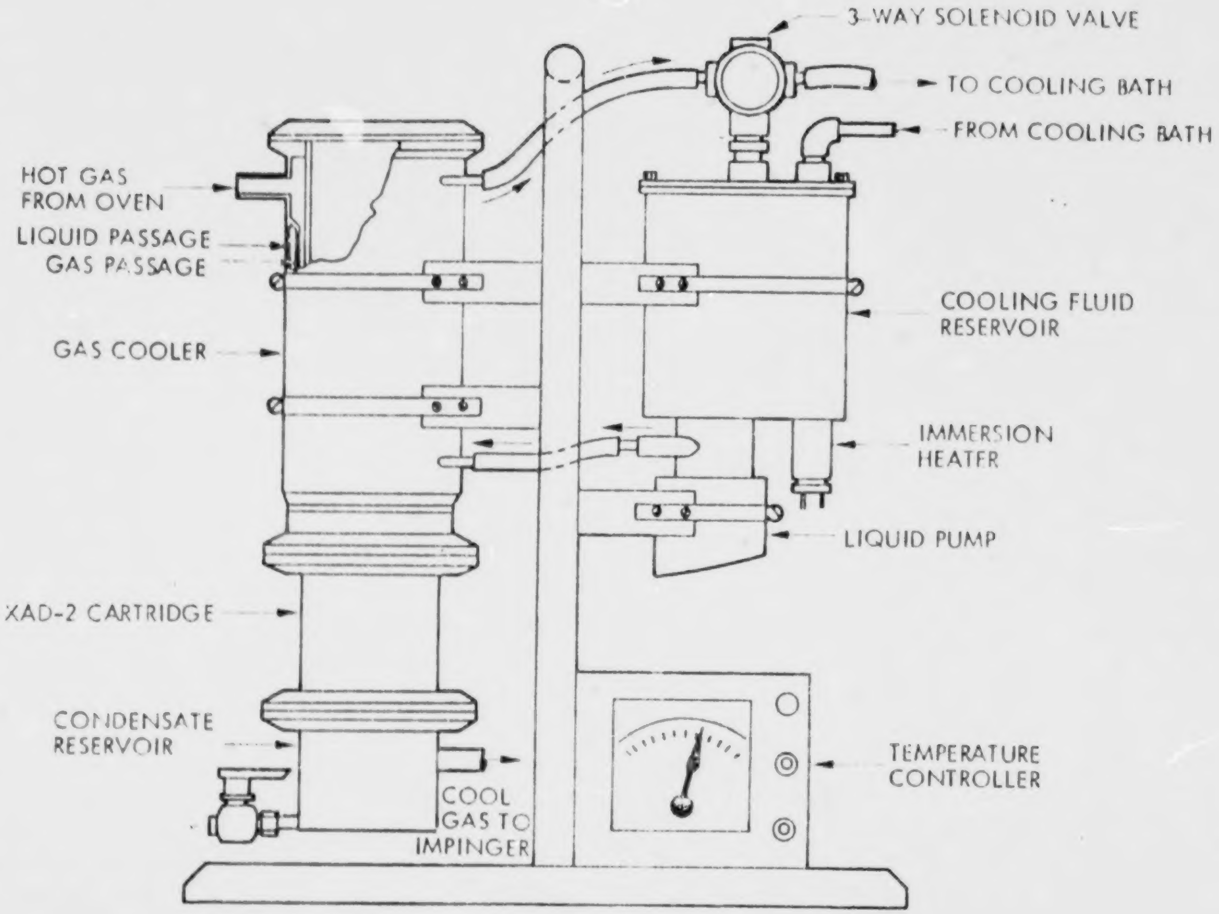

FLOW DIRECTION
8-MM GLASS COOLING COIL
XAD-2 ADSORBENT
THERMOCOUPLE
28/12 SOCKET
GLASS WATER JACKET
GLASS FRITTED DISC
GLASS WOOL PLUG
28/12 SOCKET

Figure 2. Schematic of sorbent trap.


HEATER CON-TROLLER
CONVECTION OVEN
FILTER
GAS COOLER
STACK T.C.
SS PROBE
10µ
3µ
1µ
GAS TEMPERATURE T.C.
S-TYPE PITOT
0—5
0—4
OVEN T.C.
XAD-2 CARTRIDGE
CONDENSATE COLLECTOR
IMP/COOLER TRACE ELEMENT COLLECTOR
IMPINGER T.C.
DRY GAS METER ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
10 CFM VACUUM PUMP

Source: EPA 600/2-76-160a, June 1976, p. 30.

Figure 3. SASS train schematic.


3-WAY SOLENOID VALVE
TO COOLING BATH
FROM COOLING BATH
HOT GAS FROM OVEN
LIQUID PASSAGE
GAS PASSAGE
COOLING FLUID RESERVOIR
GAS COOLER
IMMERSION HEATER
LIQUID PUMP
XAD-2 CARTRIDGE
CONDENSATE RESERVOIR
COOL GAS TO IMPINGER
TEMPERATURE CONTROLLER

Source: EPA-600/2-76-160a, June 1976, p.32.

Figure 4. XAD-2 sorbent trap module.

Trace organic material not collected by the XAD-2 resin trap passes into a bank of four ice-cooled impingers. The first impinger contains 500-mℓ HPLC grade H_2O to serve as a cold trap. The second and third impingers are empty for additional H_2O trapping capacity. The final impinger contains 750 grams of silica gel to prevent the entry of moisture into the pump.

The SASS train was operated on the stack at Facility A only to collect a sample volume of 30 standard m^3 (1060 scf) at a rate of 4 scf/min. The train was operated for a period of approximately 5 hr and was leak checked before and after the sampling runs. The sampling procedures followed are specified in the SYSTECH Test Protocol[6] and the SASS Train Manual.[7]

Combustion air sampling program--In order to characterize the air used in combustion in terms of its trace organic composition, SYSTECH employed two sampling methods appropriate for the goals of this program. With the first method, vaporous trace organics were collected with a sampling train incorporating an XAD-2 resin trap followed by a bank of impingers for condensate collection (see Figure 5). Particulates and trace organic compounds adsorbed to these particles were collected by the second sampling method on a glass fiber filter with a General Metal Works Hi-Vol sampler (see Figure 6). These methods were designed at the direction of the EPA/OSW to collect samples similar to those derived from the Modified Method 5 trains used in the source sample collection program. Results obtained from the combustion air analysis should therefore be directly comparable with those obtained from the analysis of facility emissions.

Both sampling systems were placed as near as possible to the forced draft fan intake of the combustion system. Since the goal of this program was to characterize the actual combustion air, no attempt was made to eliminate the entry of recirculated stack gases, plant dust, etc., into the sampling trains. This approach should not be interpreted as an ambient sampling program because it was not designed to characterize the environment surrounding the facility.

Sampling program quality assurance--Field sampling method blanks were performed in conjunction with each of the test efforts. These blanks consisted of assembling the sampling trains in the designated sample recovery areas and sampling room air through a chromatography grade charcoal filter. Because of the difficulties involved in filtering input air to the Hi-Vol samples no air was drawn through this combustion air sampling system for method blanks. At the end of the sampling periods, the trains were disassembled and samples were recovered as specified in the SYSTECH Test Protocol.[6]

The objectives of these method blanks were to provide a reference blank against which field samples could be compared. If analysis of the blanks indicated no significant concentrations of TCDDs and TCDFs, it was assumed that the trains, XAD-2 resin, solvents, and recovery methods did not introduce any contaminants into the field samples. In the event that the sampling method blanks did indicate the presence of contaminants, back-up field and

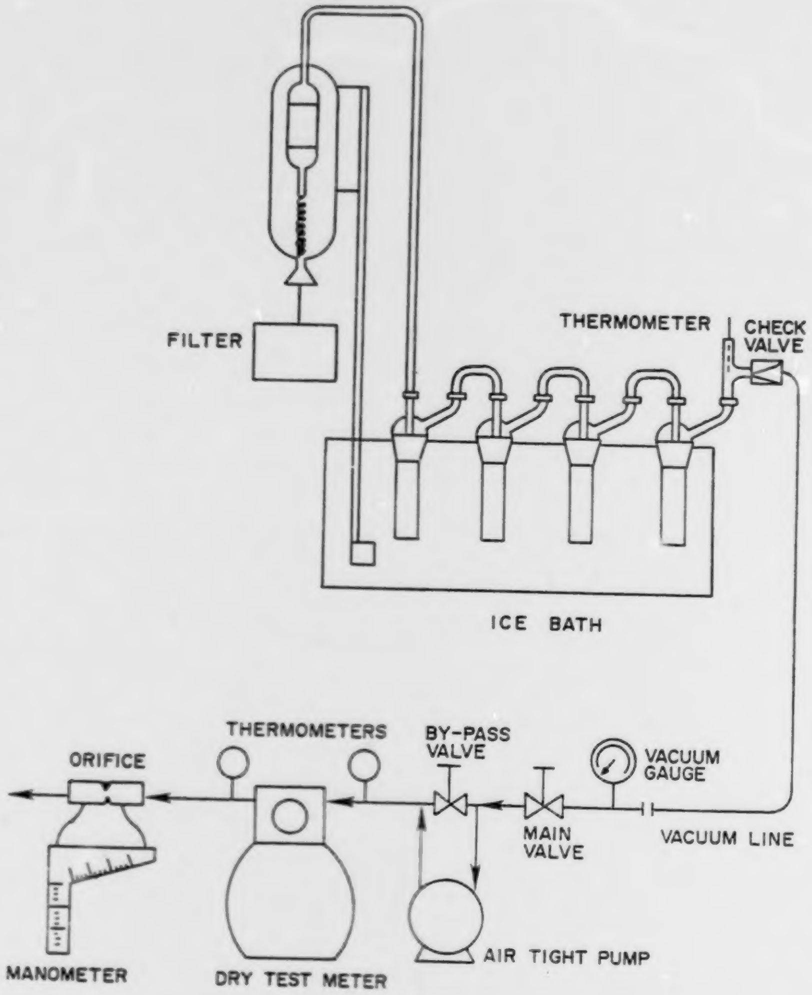

FILTER
THERMOMETER
CHECK VALVE
ICE BATH
THERMOMETERS
ORIFICE
BY-PASS VALVE
VACUUM GAUGE
MAIN VALVE
VACUUM LINE
MANOMETER
DRY TEST METER
AIR TIGHT PUMP

Figure 5. Resin collection system.

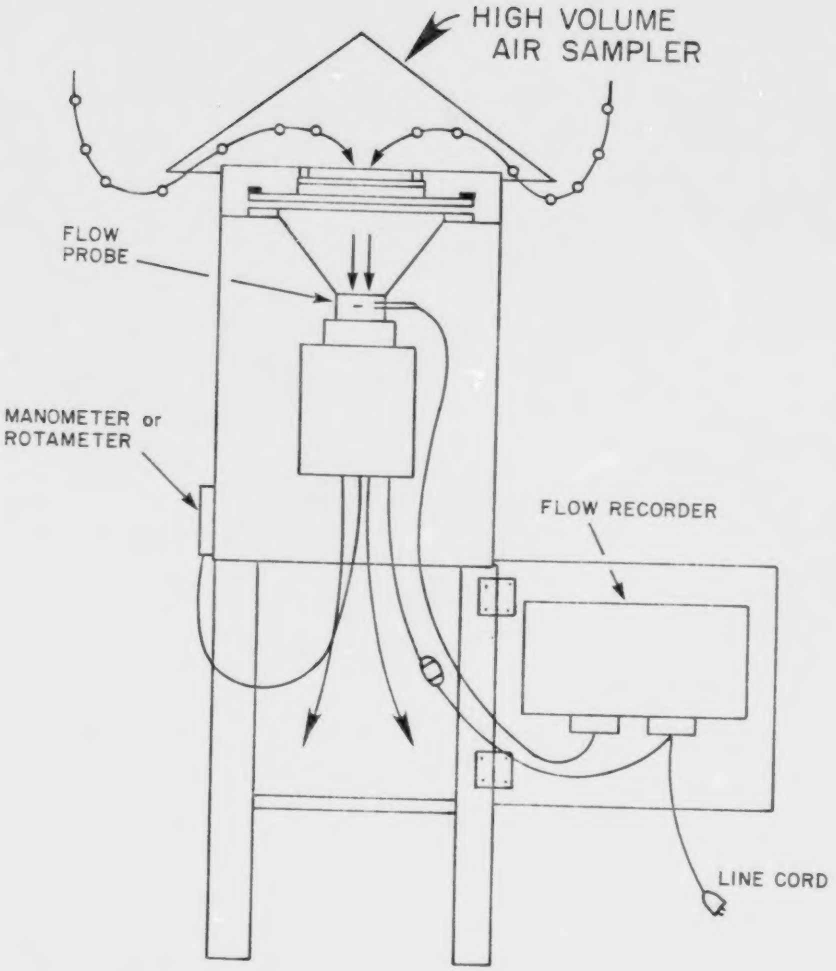

HIGH VOLUME
AIR SAMPLER
FLOW
PROBE
MANOMETER or
ROTAMETER
FLOW RECORDER
LINE CORD

Figure 6. Combustion air sampler.

laboratory samples of filters, XAD-2 resin, and solvents were available for further analyses.

Analysis Program

A prioritized sample analysis program was employed to obtain the maximum possible amount of information from the samples collected in this program. All stack samples and sampling method blanks collected were analyzed for total TCDDs and total TCDFs. Appropriate analytical blanks and standards were included in this analysis. A subset of these samples was then identified for isomer specific analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF. When these two data sets indicated the need for further documentation of results, subsets of the process stream samples and combustion air samples were designated for analysis. In this manner, support samples were analyzed only when the initial analysis of stack samples indicated the need for further examination.

Sample Preparation--

Methods of sample preparation are described in Appendix B. In general, analytical samples were recovered from the field samples either by Soxhlet extraction or simple solvent extraction. Extraction was followed up by liquid chromatography employing silica and alumina columns. Samples were concentrated and stored at -4°C for analysis. Analytical method blanks were also carried through the sample preparation phase and subsequently analyzed at a frequency of 1 per every 5 samples.

Total TCDDs and TCDFs--

Samples were analyzed for total TCDDs and total TCDFs by GC/HRMS. A detailed discussion of this procedure is included in Appendix B. The samples were analyzed by a Kratos MS-50 ultra-high resolution mass spectrometer interfaced via a jet separator to a Perkin Elmer Sigma II gas liquid chromatograph. Packed-column chromatography was used in this analysis, permitting the identification of TCDDs and TCDFs as either pre-elutors or co-elutors of the 2,3,7,8 isomers. For TCDD, the ions of m/z 321.8936 (the most abundant molecular ion having natural isotopic elemental abundances) and m/z 333.9339 (^{13}C-2,3,7,8-TCDD, the internal standard) were observed. The ion of m/z 319.8965 was also monitored for some of the TCDD analyses. For the TCDF analyses, a second aliquot of sample was monitored for the internal standard m/z 333.9339 (^{13}C-2,3,7,8-TCDD) and for m/z 305.8986 (the most abundant molecular ion having natural isotopic abundances). For some TCDF analyses, the ion of m/z 303.9016 was also monitored.

Quantification of both TCDDs and TCDFs was achieved using the internal standard ratio method. Throughout the experiment, standard samples containing 2,3,7,8-TCDD or 2,3,7,8-TCDF and ^{13}C-2,3,7,8-TCDD were analyzed. The slopes of the calibration plots were taken as the averages of the ratios of $(I^{334}/ng)/(I^{322}/ng)$ (I is the normalized intensity for the designated mass) for TCDD and $(I^{334}/ng)/(I^{306}/ng)$ for TCDF obtained using the standard samples. Residues of TCDD or TCDF in actual samples were calculated by comparing the ratios of intensities of I^{322}/I^{334} (for TCDD) and I^{306}/I^{334} (for TCDF) obtained for a given sample with the slope of the calibration plot. The detection limit was considered to be the respective value obtained for a intensity of 2.5 × noise level measured at the base line.

The internal standard (^{13}C-2,3,7,8-TCDD) was utilized in the calculation of percent recoveries, and in doing so the absolute intensity (I^{334} normalized) was measured and compared with the intensities (I^{334}/ng) obtained by injecting standard solutions of the internal standard. The recovery for TCDF was assumed to be identical to that for TCDD according to this calculation method.

Isomer Specific TCDD and TCDF Analysis--

Appropriate dilutions of the samples were made at the time of analysis and the aliquots from the resulting solutions were used for capillary column GC/HRMS. A detailed description of this procedure is included in Appendix B. A Kratos MS-80 medium resolution mass spectrometer (ultimate resolution 20,000), equipped with a 5 channel multiple peak monitoring (MPM) device was used. The mass spectrometer was coupled to a Carlo-Erba gas chromatograph. The gas chromatograph was equipped with an SE-54 fused silica capillary column (0.25 mm × 30 m) which was coupled directly with the ion source.

For the TCDD analysis, the ions m/z 319.8965, m/z 321.8936 and m/z 333.9339 (^{13}C-2,3,7,8-TCDD) were monitored on three channels. The instrument was tuned using m/z 330.9792 of PFK, and this ion was used as a check mass on Channel 4. For the TCDF analysis, m/z 303.9016, m/z 305.8986, and m/z 333.9339 were monitored on 3 channels of the MPM. The instrument was tuned using the PFK m/z 304.9824 which was used as a check mass.

The absolute amounts of each isomer present were calculated by multiplying the fraction of any given isomer present (either TCDD or TCDF) by the value of the total concentration (for TCDD or TCDF) determined in the packed column analyses. The peak height of m/z 322 was used in estimating the percentage (fraction) of any given isomer present in TCDD analysis. Similarly, m/z 306 was used for this purpose in the TCDF analysis. The percentage of any given isomer represents the fraction of the isomer in question (as represented by the peak height of m/z 322 or m/z 306 for TCDD and TCDF respectively) compared with the sum total of all the peak heights detected. The retention times of the isomers were measured from the point of injection and normalized to the position of the signal of the internal standard, ^{13}C-2,3,7,8-TCDD.

Dispersion Modeling Program

The results of the total TCDD analyses of stack samples collected in this program were analyzed by EPA's PTMAX computer dispersion model. This model performs an analysis of the maximum short term ground level concentrations resulting from point source emissions as a function of atmospheric stability class and wind speed.[8] The objective of this analysis was to translate the results from the total TCDD analyses into a data set more useful in interpreting the impact of TCDD emissions on the environment.

SUMMARY OF RESULTS

The major conclusions of this program are the following:

- The analytical results of method blanks and analytical controls attest to the validity of the TCDD and TCDF data obtained in this test program.
- The emission rates of TCDDs and TCDFs from the three test facilities ranged from 10^{-9} g/sec to 10^{-7} g/sec and 10^{-8} g/sec to 10^{-6} g/sec, respectively. Because of the limited scope of the testing program, comparisons between the data obtained at the three test facilities must be made with caution.
- The emission rates of TCDDs were analyzed by the EPA PTMAX dispersion model to determine maximum 1-hr expected ground level concentrations. The results of this analysis predicted maximum ground level concentrations of TCDDs on the order of 10^{-13} to 10^{-12} g/m^3.
- The results of packed column and capillary column analyses of TCDDs and TCDFs showed that packed column GC/HRMS provides a useful "worst case" assessment of the amounts of 2,3,7,8 isomers present.

SECTION 2

TEST FACILITY DESCRIPTIONS

PROCESS DESCRIPTIONS

The facilities tested in this program are all continuously operating combustion systems designed to recover energy from solid waste either as steam or hot water. Facility A, the small modular incinerator, consists of four 25 ton per day (TPD) municipal refuse incinerator units combined with heat recovery equipment to produce steam. The field erected incinerator and recovery system, Facility B, is designed to burn 40 to 50 TPD of municipal refuse and waste oil and reclaim available energy as steam. Facility C is an industrial spreader stoker system which generates high temperature hot water (HTHW). Facility C burned 50 to 70 TPD of densified refuse derived fuel (dRDF) or 30- to 35-TPD coal during the test periods. Process descriptions of these facilities are outlined as follows.

Facility A

During the tests conducted at Facility A, both as-received and trommeled refuse were burned in the incinerator. Mass flows of refuse into the incinerator were determined by recording the weights of trucks delivering refuse to the facility and removing that portion of the refuse rejected by the trommel. Refuse is combusted at Facility A in a two-chambered incinerator module, shown in the schematic in Figure 7. A multiple hydraulic ram system pushes the waste down a terraced hearth into and through the primary combustion chamber. This chamber is operated at approximately 690°C (1200°F) to maintain substoichiometric conditions. The temperature in the secondary chamber is kept between 980°C and 1010°C (1800° and 1850°F) by modulating the air into the primary and secondary chambers.

Two rams in the hearth of the primary chamber are cycled to push the residue forward and to break up clinker formations. A residue removal ram is automatically cycled after several loading cycles. As the residue falls into the wet sump, it is sprayed with water. After a delay period, the drag chain lifts the residue from the sump and deposits it into the residue removal container. The mass flow of residue was determined by recording the weights of trucks removing wet residue from the facility and applying the results of the residue moisture analysis.

The incinerator system is connected to a water-tube waste heat boiler with a soot blowing system. Flue gases from the incinerator pass through a heat exchanger system consisting of five banks of vertical water tubes. The

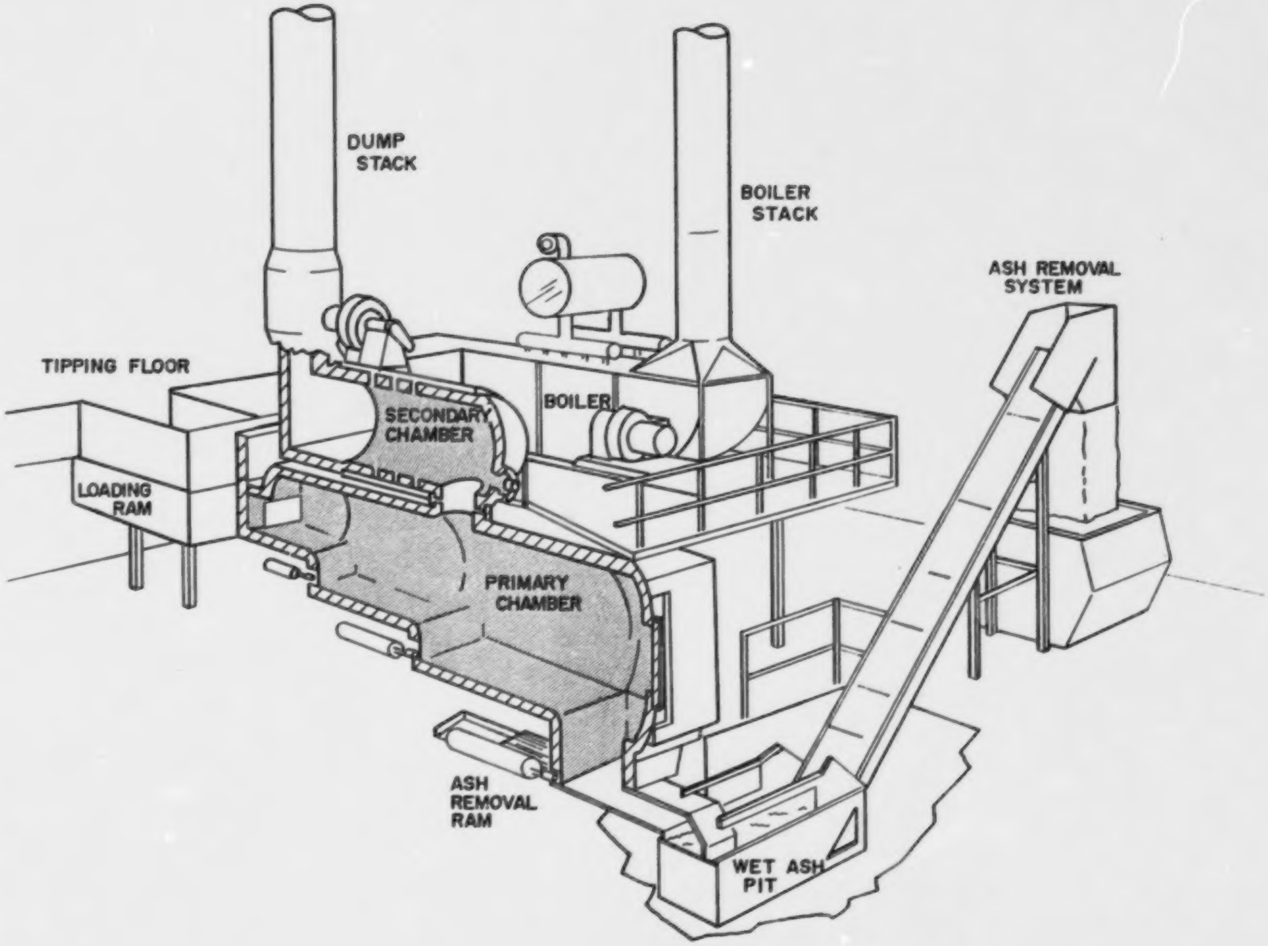

DUMP STACK
BOILER STACK
ASH REMOVAL SYSTEM
TIPPING FLOOR
SECONDARY CHAMBER
BOILER
LOADING RAM
PRIMARY CHAMBER
ASH REMOVAL RAM
WET ASH PIT

Figure 7. Three-dimensional drawing of incineration/heat recovery module at Facility A.

combustion gases are drawn slowly through the water-tube heat exchanger by an aspirator fan and cooled to approximately 600°F. Saturated 150 psi steam is produced in the heat exchanger. During steam production, a cap at the base of the dump stack is pneumatically closed, and the flue gases exit through the boiler stack. When the steam demand is reduced or the boiler system malfunctions, the hot flue gases are automatically discharged from the boiler directly into the dump stack.

Facility B

Facility B consists of a tipping floor, an open storage pit, an overhead clamshell crane, an incinerator-boiler unit, and a flue gas handling system (including a cyclone dust collector). The incinerator boiler unit is shown in schematic in Figure 8. The crane operates by radio control and transfers refuse from the storage pit to the incinerator feeder. Load cells built into the tram rail provide a weight measurement of the refuse to be dropped into the incinerator.

The incinerator feed system consists of a ram feeder-hopper assembly. The feeder ram automatically pushes the refuse from the hopper into the furnace at a rate that is compatible with the furnace capacity. Refuse, compacted by the ram feeder, enters the primary furnace chamber through the charging opening. The refuse is dried and ignited on an inclined refractory hearth located just inside the water-cooled throat. The dried refuse is forced off this hearth by the successive loading action of the feed ram. An oil-fired burner is provided in one of the primary furnace sidewalls about 3 ft from the charging opening to ignite the refuse as it enters the furnace and to aid in drying wet refuse (if required). The burner is equipped with a continuous gas pilot so that waste oil may be burned at any time. The primary combustion chamber is designed to liberate 20×10^6 Btu/hr. This liberation is equivalent to 2 tons per hour (TPH) of the municipal waste having a heat content of approximately 5000 Btu/lb.

By the time the refuse has advanced the length of the hearth, it is dried, ignited, and partially burned. It is then pushed off the hearth, and it tumbles several feet down to the stoker grate. After proceeding down the stoker grate, the burned-out ash and noncumbustible materials drop off the end of the grate into a large tank of water which serves to quench and cool the ash residue. A continuous drag flight conveyor collects the ash residue at the bottom of the tank and moves it up an elevating incline to the unloading point. The ash then drops into an open-top container. The mass flow of ash was measured by recording the weights of containers removed from the facility and applying the results of the residue moisture analysis.

The gaseous products resulting from the combustion of the refuse pass over the bridge wall at the far end of the primary combustion chamber and are immediately forced downward by an air-cooled refractory baffle into the secondary combustion chamber. Another oil burner is located in the sidewall of the bridge wall-baffle passage, spaced relatively close to the bridge wall. While this afterburner is primarily intended as a means of recovering energy from waste oil, it also serves to achieve complete combustion of the gases

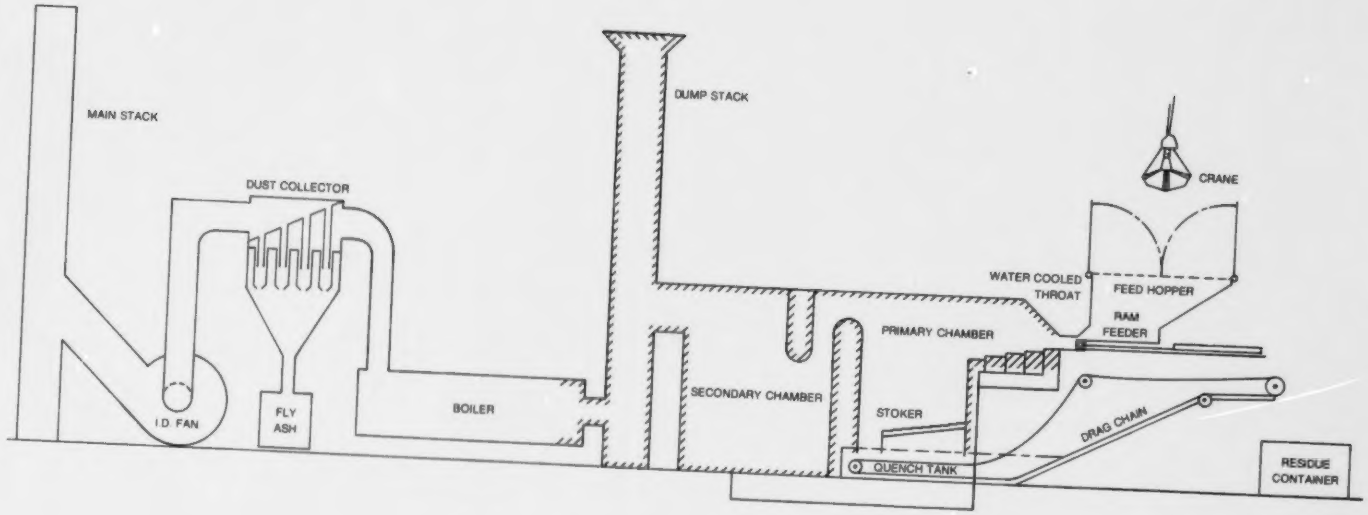

MAIN STACK
DUST COLLECTOR
I.D. FAN
FLY ASH
BOILER
DUMP STACK
SECONDARY CHAMBER
PRIMARY CHAMBER
STOKER
QUENCH TANK
WATER COOLED THROAT
FEED HOPPER
RAM FEEDER
CRANE
DRAG CHAIN
RESIDUE CONTAINER

Figure 8. Cross section of incineration/heat recovery system at Facility B.

from the primary chamber. The mixed products of combustion from the primary chamber and the afterburner are detained in the large refractory-lined secondary combustion chamber for an average of 3 seconds to ensure completion of the combustion process and to allow settling out of the large particulate.

From the secondary chamber, the combustion products enter a waste heat recovery fire tube boiler. The furnace gases, having been cooled to approximately 500°F in passing through the waste heat boiler, flow through a multiple cyclone dust collector for the removal of fine dust particles. The dust is discharged periodically through a damper into an ash container. Flue gases exiting the dust collector next pass through an insulated steel breeching to an induced draft (ID) fan. The discharge from the ID fan is connected to the main stack through a short breeching. A second stack, a flue gas dump stack, is located between the secondary combustion chamber and the boiler inlet. This dump stack is utilized when there is no need to generate steam or if there is a maintenance problem in the boiler, air pollution control, or fan systems. The dump stack has a cap that is held closed during normal operation and opens when one of the aforementioned situations occur.

Facility C

Facility C has an industrial type spreader stoker fired HTHW generator. This boiler shown in schematic in Figure 9 was operated during the tests while firing coal or dRDF separately. Fuel input was measured by a dump loader scale located between the bunker and the feed chutes of the stoker. The waterwall furnace of this system is fired by a rotograte spreader stoker. Since the unit generates high temperature hot water, there is not a separate economizer section. Combustion air is preheated by the exhaust flue gases through a gas-to-gas heat exchanger. Particulate emissions are controlled by a multiclone dust collector and an electrostatic precipitator. The unit has the capacity to transfer 100×10^6 Btu/hr. However, during the testing the unit was operated at a nominal 30×10^6 Btu/hr.

SYSTEM PERFORMANCE

In order to characterize the performance of the facilities, samples and data were collected to describe fuel properties, to quantify mass flow rates through the units, and to document the performance of the combustion units. Details of the procedures employed for this characterization are included in SYSTECH Test Protocol.[6]

Fuel Characteristics

Table 3 illustrates the ultimate analysis and heat content of the fuels burned at the test facilities. Facility A burned both as-received refuse and trommeled refuse during the test periods. The trommeled fuel differed from the as-received refuse primarily in its lower ash content and higher heat content. Facility B co-fired as-received refuse and waste oil during the tests. The waste oil was primarily fuel oil containing unknown contaminants. Facility C burned coal and dRDF during separate test periods.

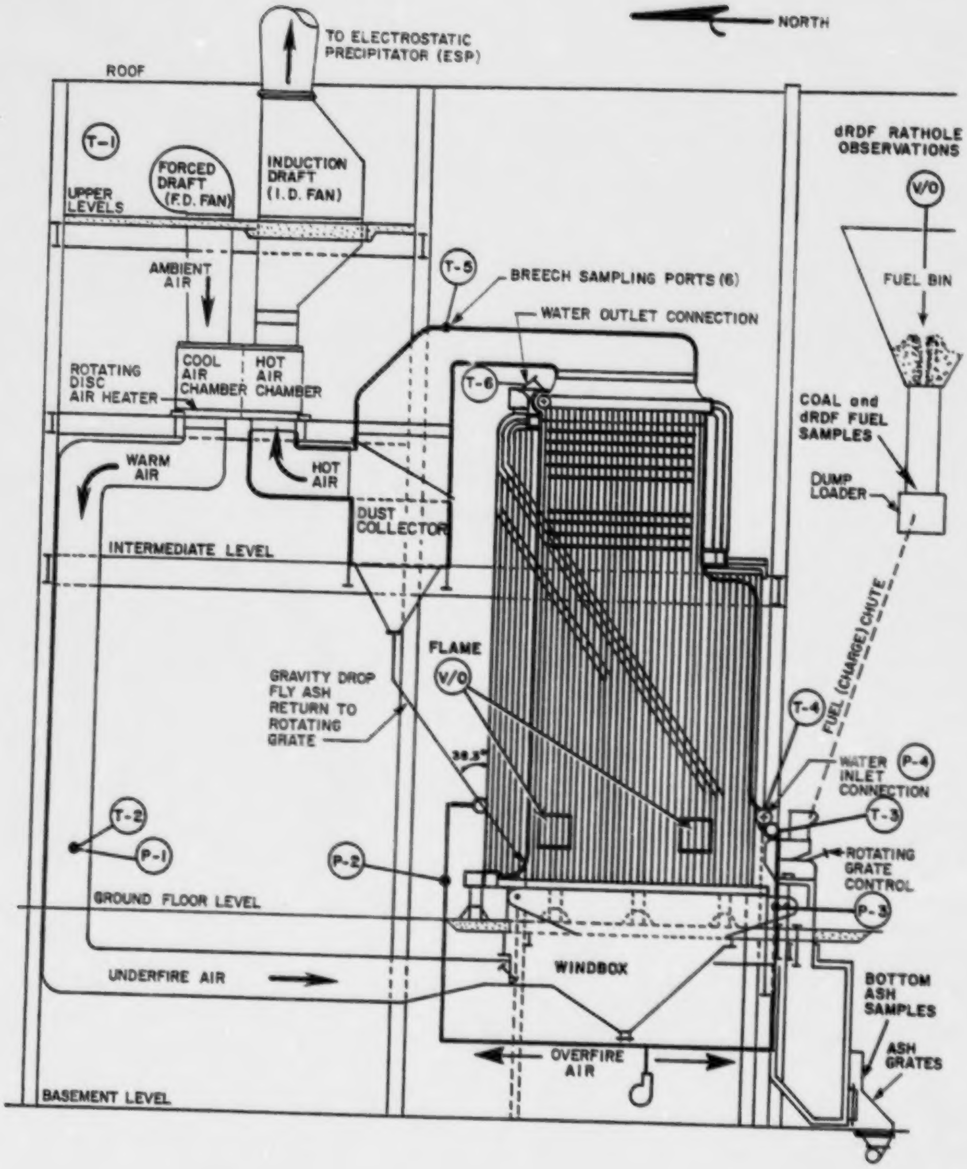

NORTH
TO ELECTROSTATIC PRECIPITATOR (ESP)
ROOF
T-1
FORCED DRAFT (F.D. FAN)
INDUCTION DRAFT (I.D. FAN)
UPPER LEVELS
dRDF RATHOLE OBSERVATIONS
V/O
FUEL BIN
AMBIENT AIR
T-5
BREECH SAMPLING PORTS (6)
WATER OUTLET CONNECTION
ROTATING DISC AIR HEATER
COOL AIR CHAMBER
HOT AIR CHAMBER
T-6
COAL and dRDF FUEL SAMPLES
WARM AIR
HOT AIR
DUMP LOADER
DUST COLLECTOR
INTERMEDIATE LEVEL
FUEL (CHARGE) CHUTE
FLAME
V/O
GRAVITY DROP FLY ASH RETURN TO ROTATING GRATE
T-4
39.5°
WATER INLET CONNECTION
P-4
T-3
T-2
P-1
P-2
ROTATING GRATE CONTROL
P-3
GROUND FLOOR LEVEL
WINDBOX
UNDERFIRE AIR
BOTTOM ASH SAMPLES
ASH GRATES
OVERFIRE AIR
BASEMENT LEVEL

Figure 9. Cross section of boiler at Facility C.

TABLE 3. FUEL PROPERTIES*

	Ultimate analysis								
Test facility	C (%)	H (%)	O (%)	N (%)	Cl (%)	S (%)	Inerts (%)	Moisture (%)	Heat content (Btu/lb)
Facility A									
As-received refuse	27.7	4.4	20.5	0.4	--	0.1	24.5	22.4	4,541
Trommeled refuse	32.2	4.9	23.7	0.3	--	0.1	15.0	23.8	5,416
Facility B									
As-received refuse	28.98	3.83	20.35	0.61	0.56	0.16	20.36	25.1	5,134
Waste oil†	86	12	--	--	--	0.5	--	<0.2	19,753
Facility C									
dRDF	44.23	5.60	35.99	0.34	--	0.21	9.65	11.42	7,164
Coal	79.60	5.14	5.97	1.66	--	0.67	5.54	5.03	13,051

* As-fired basis.

† Estimated.

Table 4 summarizes the results of the refuse characterization for Facilities A and B. It is apparent that the trommeled refuse burned at Facility A is enriched in paper and plastic in comparison with the as-received fuel from which it was derived. The as-received refuse burned at both Facility A and B were typical of normal municipal refuse composition.

Mass Flow Rates

Table 5 summarizes the mass flow rates of feed, ash, and flue gas observed at the test facilities. The flue gas flow rates were determined from the fuel ultimate analysis, observed excess air levels, and measured mass flow rates of feed and ash. An example of the calculation procedure is included in Appendix C. Both the fuel and flue gas mass flow rates were used to quantify the emission rates of the TCDDs and TCDFs. The mass flow rates for the tests conducted at Facility A were determined as test period averages, while those for Facilities B and C were determined as daily averages.

TABLE 4. REFUSE CHARACTERIZATION*

Category	Weight Percent by Category		
	Facility A		Facility B
	Trommeled	As-received	As-received
Paper	68.5	49.7	44.7
Organic	5.5	10.7	11.7
Wood	1.1	0.9	3.1
Iron	5.4	5.9	5.3
Aluminum	0.9	1.6	1.0
Metals	0.8	0.5	1.4
Glass	2.8	8.8	4.4
Plastic	8.1	6.9	4.4
Textile	5.0	3.3	10.4
Inerts	0.2	0.4	6.6
Fines	1.7	11.3	1.5

* As-fired basis.

TABLE 5. MASS FLOW RATES*

Facility	Date	Type fuel burned	Mass flow rates			
			Feed lb/hr	Ash† lb/hr	Flue gas lb/hr dry	Flue gas DSCFM
A	09-16-80	Trommeled refuse	3,120	455	56,434	11,840
	09-18-80	Trommeled refuse	3,120	455	56,434	11,840
	10-22-80	As-received refuse	4,240	1,093	67,706	14,119
	10-23-80	As-received refuse	4,240	1,093	67,706	14,119
B	12-08-80	As-received refuse Waste oil	2,147 400 2,547	162	41,052	8,514
	12-09-80	As-received refuse Waste oil	2,000 313 2,313	432	36,983	7,670
	12-10-80	As-received refuse Waste oil	1,982 326 2,308	776	36,563	7,583
C	04-01-81	dRDF	4,615	413	68,030	14,754
	04-07-81	Coal	2,731	117	78,920	17,145

* Feed and ash on as-fired basis.
† Ash on dry basis.

Process Operations

Table 6 summarizes the process operations data recorded during the tests. The excess air levels recorded on this table were used in calculating emission rates. System temperatures were recorded to provide information regarding the combustion processes occurring at the facilities. The particulate emissions survey was conducted to characterize the performance of the systems. It should be noted that although particulate emissions from Facilities A and B are relatively high, neither facility is subject to federal regulation because of their small size.

TABLE 6. PROCESS OPERATIONS DATA

			Operating data						
			Excess air level		System temperatures (°F)				Particulate emissions
Facility	Date	Type fuel burned	Boiler outlet (%)	Stack (%)	Primary	Secondary	Boiler outlet	Stack	gr/scf*
A	09-16-80	Trommeled refuse	155	302	1599	1605	582	375	.218
	09-18-80	Trommeled refuse	155	302	1599	1605	582	375	.218
	10-22-80	As-received refuse	172	308	1322	1834	573	409	.199
	10-23-80	As-received refuse	172	308	1322	1834	573	409	.199
B	12-08-80	As-received refuse and waste oil	150	187	996	1494	463	427	.669
	12-09-80	As-received refuse and waste oil	150	187	1193	1578	470	434	.669
	12-10-80	As-received refuse and waste oil	150	187	1173	1557	467	439	.669
C	04-01-81	dRDF	†	160	†	†	302	303	.005
	04-07-81	Coal	†	169	†	†	306	306	.006

* Corrected to 12 percent CO_2.

† No data was available.

SECTION 3

TRACE ORGANIC DATA

STACK EMISSIONS

The data generated from stack samples collected during this program are shown in detail in Appendix C and summarized in this Section. In the data tables the sign < is employed to indicate the instrumental detection limit when no TCDD or TCDF was actually detected in the sampling train components. Totals for samples which contained components with no detectable levels of TCDD or TCDF have been expressed as ranges. The lower ends of the ranges represent the amounts actually detected in the samples while the upper ends include the amount actually detected plus the detection limits of those components in which none was detected. The concentrations of TCDDs and TCDFs detected by packed column GC/HRMS in stack samples are first compared to those observed for sampling method blanks. The TCDD and TCDF data are then presented as emission rates. Finally, the concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF as determined by capillary column GC/HRMS are compared to those indicated by the packed column GC/HRMS analyses.

Sampling Method Blanks

Table 7 illustrates the concentrations of TCDDs and TCDFs detected by packed column GC/HRMS in sampling method blanks and stack samples taken during this program. Results are presented in terms of concentrations of total TCDDs and total TCDFs and in terms of maximum concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF. These latter concentrations are termed "maximum" because they also include isomers of TCDDs and TCDFs which co-elute (are not chromatographically separable from) with the 2,3,7,8 isomers in packed column analysis.

It is apparent from Table 7 that the sampling method blanks contained far less TCDDs and TCDFs than stack samples taken during the same test periods. In most cases, the amounts of TCDDs and TCDFs in sampling method blanks ranged from none detected to approximately 5 percent of those detected in stack samples. The amount of TCDD detected in the blank conducted at Facility B did represent a significant portion of the amount of TCDD found in stack samples. However, it is suspected that this blank may have been inadvertently contaminated in sampling or during recovery from the sampling train. Furthermore the recovery operation was performed in the waste oil analysis lab at Test Facility B, which was heavily contaminated with waste oil vapors. Since combustion air blanks taken at Facility B and XAD-2 reference

TABLE 7. COMPARISON OF STACK SAMPLES AND SAMPLING METHOD BLANKS FOR TCDD AND TCDF CONCENTRATIONS

			TCDD		TCDF	
Facility sample type	Date	Sampling train	Total TCDD (pg/m^3)	Maximum 2,3,7,8-TCDD (pg/m^3)	Total TCDF (pg/m^3)	Maximum 2,3,7,8-TCDF (pg/m^3)
Facility A						
Blank	09-12-80	SASS	<30	<30	*	*
Stack	09-16-80	SASS	8,400 ±10	3,500	*	*
Stack	10-23-80	SASS	1,400	310	17,000	6,000
Blank†	10-15-80	MM5	<57	<25	<120§	<40§
Stack	09-18-80	MM5	1,100	290	14,000	7,900
Stack	10-22-80	MM5	1,300	300	8,300	2,800
Facility B						
Blank	12-05-80	MM5	1,060	130	160 ±97	93 ±32
Stack	12-08-80	MM5	4,400	2,700	47,700	24,000
Stack	12-09-80	MM5	3,800	1,200	4,500	1,900
Stack	12-10-80	MM5	2,500	1,100	10,900	4,900
Facility C						
Blank	02-27-81	MM5	920	370 ±10	<120	<53
Stack	04-01-81	MM5	30,000	9,600	312,000	114,000
Stack	04-07-81	MM5	29,500	8,600	247,000	85,000

* Samples not analyzed.

† Concentrations computed from average volume drawn through stack trains on 9-18-80 and 10-22-80 (4.98 dscm).

§ These figures do not include TCDF measured in the resin which was determined to be an analytical artifact resulting from carry-over of column residue from the previous injection.

blanks (discussed later in this section) did not show significant levels of TCDDs and TCDFs, it was decided not to reject the stack data.

The results of these method blanks indicate that, in general, no major portion of the amounts of TCDDs and TCDFs detected in stack samples can be attributed to either the sampling trains or sampling methods. Because only very small amounts of TCDDs and TCDFs were found in the blanks, with the exception of Facility B as noted earlier, the stack sample results have not been corrected for the contribution of the blanks.

Analytical Method Blanks and Standards

During the analysis of samples in this program, method blanks and appropriate standards were analyzed during each analysis period. Method blanks were analyzed at a frequency of 1 per every 5 samples. The results of these analyses are included in Appendix C with the stack sample test run results. No detectable amounts of TCDD or TCDF were found in any of the method blanks analyzed, with the exception of three instances noted in Tables 1A and 1B in Appendix C. The amounts of TCDD or TCDF indicated in these instances were either only slightly above detection limits or else attributable to column carry-over from previously analyzed samples.

Total TCDDs and TCDFs in Stack Samples

Table 8 presents the results of the total TCDD and TCDF analyses conducted in this program in terms of g/sec emission rates. There was no significant difference at a 95 percent confidence level (Student's t-test, variances not assumed equal) between the emission rates (g/sec) of total TCDDs and TCDFs observed at Facility A and Facility B. Although the emission rates observed at Facility C appear considerably higher than any of the emission rates observed at Facilities A or B, insufficient samples were taken to determine whether this difference was statistically significant. Table 9 presents the emission rates on a g/ton fuel fired basis. No significant difference at a 95 percent confidence limit (Student's t-test, variances not assumed equal) was found between the emission rates on a g/ton basis at Facilities A and B. Again, more samples would be required to determine whether the emissions observed at Facility C were significantly higher than those at Facilities A and B.

An analysis of the data obtained at each facility indicates some interesting observations regarding emission rates and fuel type burned. First, there was no significant difference at a 95 percent confidence limit (Student's t-test, variances not assumed equal) between TCDD and TCDF emissions measured while burning as-received and then trommeled refuse at Facility A. This observation indicates that the differences in fuel properties between as-received and trommeled refuse reported in Section 2 are not reflected in emissions.

The data obtained at Facility B indicate a positive relationship between the waste oil fraction of the fuel burned and the emissions of TCDFs. Key information in interpreting this relationship is discussed later in this section.

The data collected at Facility C indicate that TCDDs and TCDFs were emitted during the combustion of both dRDF and coal. Although more samples would be required to precisely quantify the amounts emitted, the results of

TABLE 8. EMISSION RATES OF TCDD AND TCDF (g/sec Basis)

				TCDD (g/sec)		TCDF (g/sec)	
Facility	Fuel burned	Date	Sampling train	Total	Maximum 2,3,7,8	Total	Maximum 2,3,7,8
A	Trommeled refuse	09-16-80	SASS	4.7×10^{-8}	2.0×10^{-8}	*	*
	Trommeled refuse	09-18-80	MM5	6.0×10^{-9}	1.6×10^{-9}	7.8×10^{-8}	4.4×10^{-8}
	As-received refuse	10-22-80	MM5	9.0×10^{-9}	2.0×10^{-9}	5.5×10^{-8}	1.9×10^{-8}
	As-received refuse	10-23-80	SASS	9.6×10^{-9}	2.0×10^{-9}	1.1×10^{-7}	4.0×10^{-8}
B	As-received refuse and waste oil	12-08-80	MM5	1.8×10^{-8}	1.1×10^{-8}	1.9×10^{-7}	9.7×10^{-8}
	As-received refuse and waste oil	12-09-80	MM5	1.4×10^{-8}	4.2×10^{-9}	1.6×10^{-8}	7.0×10^{-9}
	As-received refuse and waste oil	12-10-80	MM5	8.9×10^{-9}	3.8×10^{-9}	3.9×10^{-8}	1.7×10^{-8}
C	dRDF	04-01-81	MM5*	2.1×10^{-7}	6.7×10^{-8}	2.2×10^{-6}	8.0×10^{-7}
	Coal	04-07-81	MM5*	2.4×10^{-7}	6.9×10^{-8}	2.0×10^{-6}	6.9×10^{-7}

* Only one sample available

TABLE 9. EMISSION RATES OF TCDD AND TCDF
(g/ton fuel fired basis)

Facility	Fuel burned	Date	Sampling train	TCDD (g/ton) Total	TCDD (g/ton) Maximum 2,3,7,8	TCDF (g/ton) Total	TCDF (g/ton) Maximum 2,3,7,8
A	Trommeled refuse	09-16-80	SASS	1.1×10^{-4}	4.6×10^{-5}	*	*
	Trommeled refuse	09-18-80	MM5	1.4×10^{-5}	3.7×10^{-6}	1.8×10^{-4}	1.0×10^{-4}
	As-received refuse	10-22-80	MM5	1.5×10^{-5}	3.4×10^{-6}	9.4×10^{-5}	3.2×10^{-5}
	As-received refuse	10-23-80	SASS	1.6×10^{-5}	3.5×10^{-6}	1.9×10^{-4}	6.8×10^{-5}
B	As-received refuse and waste oil	12-08-80	MM5	5.1×10^{-5}	3.1×10^{-5}	5.4×10^{-4}	2.7×10^{-4}
	As-received refuse and waste oil	12-09-80	MM5	4.4×10^{-5}	1.3×10^{-5}	5.0×10^{-5}	2.2×10^{-5}
	As-received refuse and waste oil	12-10-80	MM5	2.8×10^{-5}	1.2×10^{-5}	1.2×10^{-4}	5.3×10^{-5}
C	dRDF	04-01-81	MM5*	3.3×10^{-4}	1.0×10^{-4}	3.4×10^{-3}	1.2×10^{-3}
	Coal	04-07-81	MM5*	6.3×10^{-4}	1.8×10^{-4}	5.3×10^{-3}	1.8×10^{-3}

* Only one sample available

the sampling method blank (see Table 7) analyzed for this test period indicate that these data are valid. The presence of TCDDs and TCDFs in stack samples from coal combustion has not been clearly established in previous studies. One study has indicated the presence of polychlorinated dibenzo-p-dioxins including TCDDs in emissions from a fossil fuel fired powerhouse[1], while another has found no TCDD detected at 1.2 ppt in the stack collected fly ash of a coal fired powerhouse[9]. The implications of the results of the present study are discussed further in Section 5 of this report.

Isomer Identification and Qualification

The complete results of the capillary column GC/HRMS analysis of stack samples for TCDD and TCDF isomers are included in Appendix C. Table 10 shows a summary of the data obtained from packed column and capillary column analyses of selected samples for 2,3,7,8-TCDD and 2,3,7,8-TCDF. The amounts of 2,3,7,8 isomers reported from packed column analyses have been labeled "maximum" concentrations because they also include isomers co-eluting with 2,3,7,8 isomers. The capillary column results provide a direct determination of the actual amounts of 2,3,7,8 isomers present.

The packed column analyses for TCDD showed that an average of about 40 percent of the TCDD collected in the test program could be tentatively identified as 2,3,7,8-TCDD. Capillary column analyses confirmed that less than half the 40 percent was actually 2,3,7,8-TCDD, with the remainder being co-eluters of 2,3,7,8-TCDD. Packed column analyses for TCDF showed that about 44 percent of the TCDF collected could be tentatively identified as 2,3,7,8-TCDF. Slightly more than half the 44 percent was confirmed as 2,3,7,8-TCDF by the capillary column analyses. The remainder was co-eluters of 2,3,7,8-TCDF.

COMBUSTION AIR SAMPLES

The complete data set for combustion air samples is included in detail in Appendix C. The results of the packed column GC/HRMS analysis for TCDDs and TCDFs are summarized in Table 11.

XAD-2 Resin System

The results from the XAD-2 resin sampling system shown in Table 11 indicated that no TCDDs or TCDFs were detected at Facility B at a detection limit less than 10 pg/m^3. At Facility C, however, both TCDDs and TCDFs were detected in the sample taken during the burning of dRDF. During the coal burning test only a small amount of TCDD was detected, none of which was tentatively identified as 2,3,7,8-TCDD by packed column analysis. No TCDFs were detected during this test. Both TCDD and TCDF concentrations in combustion air samples from Facility C were approximately two orders of magnitude lower than those reported for stack samples. The significance of these results from the coal burning test are discussed further in Section 5. No combustion air samples were taken at Facility A.

TABLE 10. COMPARISON OF PACKED COLUMN AND CAPILLARY COLUMN ANALYSES OF MODIFIED METHOD 5 STACK SAMPLES FOR 2,3,7,8-TCDD AND 2,3,7,8-TCDF

Facility	Date	Fuel type	Sample type	Maximum 2,3,7,8-TCDD identified by packed column (pg/m^3)	Percent of total TCDD identified as 2,3,7,8-TCDD (%)	2,3,7,8-TCDD identified by capillary column (pg/m^3)	Percent of total TCDD identified as 2,3,7,8-TCDD (%)	Maximum 2,3,7,8-TCDF (pg/m^3)	Percent of total TCDF identified as 2,3,7,8-TCDF (%)	2,3,7,8-TCDF identified by capillary column (pg/m^3)	Percent of total TCDF identified as 2,3,7,8-TCDF (%)
A	09-18-80	Trommeled refuse	XAD-2	280	26	180	17	7,800	56	4,100	30
	10-22-80	As-received refuse	XAD-2	280	23	170	16	2,300	33	1,100	16
B	12-08-80	As-received refuse and waste oil	Probe and filter	1,100	83	200	15	7,400	48	3,800	25
	12-08-80	As-received refuse and waste oil	XAD-2	1,600	52	270	9	17,000	53	9,200	29
	12-10-80	As-received refuse and waste oil	XAD-2	900	43	270	13	4,100	46	2,400	27
C	04-01-81	dRDF	Probe and filter	37	40	12	13	350	44	170	21
	04-01-81	dRDF	XAD-2	9,500	32	3,100	11	113,000	39	59,100	20
	04-07-81	Coal	XAD-2	8,600	29			85,000	34		

TABLE 11. COMPARISON OF COMBUSTION AIR SAMPLES AND METHOD BLANKS FOR TCDD AND TCDF CONCENTRATIONS

			TCDD		TCDF	
Facility sample type	Date	Sampling train/ sample type	Total TCDD (pg/m^3)	Maximum 2,3,7,8-TCDD (pg/m^3)	Total TCDF (pg/m^3)	Maximum 2,3,7,8-TCDF (pg/m^3)
Facility B						
Blank	12-05-80	Resin/XAD-2	<10	<5	<28	<14
Waste oil + refuse test	12-08-80	Resin/XAD-2	<4	<2	<11	<3.9
"	12-09-80	Resin/XAD-2	<9	<4	<13	<5.5
"	12-10-80	Resin/XAD-2	<5	<2	<4.2	<1.3
Blank	12-07-80*	Hi-Vol/filter	<.05	<02	<.09	<.09
Waste oil + refuse test	12-08-80	Hi-Vol/filter	.31	.12	.86	48
"	12-09-80	Hi-Vol/filter	.39	.16	.84	40
"	12-10-80	Hi-Vol/filter	.24	.076	<.48	<.18
Facility C						
Blank	02-27-81	Resin/XAD-2	<14	<8.6	<9.6	<4.9
dRDF test	04-01-81	Resin/XAD-2	480	120	1,300	640
Coal test	04-07-81	Resin/XAD-2	29	<13	<53	<24
Facility C						
Blank	04-01-81†	Hi-Vol/filter	<.17	<.17	<.17	<.07
dRDF test	04-01-81	Hi-Vol/filter	<.58	<.20	.48	<.13
Coal test	04-07-81	Hi-Vol/filter	<.25	<.12	<.12	<.04

* Computed from average sample volume (2500 dscm).
† Computed from average sample volume (890 dscm).
Note: Combustion air sampling was not conducted at Facility A.

Hi-Vol System

Table 11 indicates that small concentrations of TCDDs were found in the particulate combustion air samples collected at Facility B. These concentrations were approximately four orders of magnitude less than the amount of TCDD found in stack samples. The amounts of TCDFs reported for these samples ranged from none detected to approximately five orders of magnitude lower than that observed in stack samples.

At Facility C, no TCDD or TCDF was found in the combustion air samples collected during the coal burning test. During the dRDF burning test, no TCDD was found, and only a small amount of TCDF was detected. None of the TCDF collected was identified as 2,3,7,8-TCDF.

OTHER SAMPLES

Resin Samples

Facility A was located adjacent to a wood preservative manufacturing concern which maintained large stores of pentachlorophenol (PCP) on site. Because of the implication of chlorophenols as precursors for chlorodioxin formation, the EPA Project Officer directed SYSTECH to obtain an air sample for PCP analysis. The results of analysis of this sample as the pentachloroanisole derivative of PCP are shown in Table 12. Procedures employed for this analysis are included in Appendix C.

TABLE 12. ANALYSIS OF PENTACHLOROPHENOL (PCP) AS PENTACHLOROANISOLE (PCA) IN XAD-2 RESIN SAMPLES

Sample code	Dry weight of the resin (g)*	Amount of PCA (ng)†	Detection limit (ng)	Amount of PCP (ng)
PCP-A-Resin	30	400	4	380
PCP-B-Resin	15	930	22	885
PCP-Control-Resin§	25	250	3	240

* Approximate dry weights are given.

† Amount of PCP was evaluated from PCA assuming the derivation of phenol to anisole is 100 percent.

§ PCP-Control-Resin was spiked with 2.85 ng of PCP. This is approximately 1 percent of the total PCP that was actually detected in the resin. The remainder of the PCP was apparently in the resin itself.

Resin A was an XAD-2 field blank maintained on site at Facility A. The control resin was an XAD-2 reference blank maintained at SYSTECH's Corporate Offices. The XAD-2 Resin B was used to collect an air sample at the air intake to the incinerator. The resin was loaded into a sorbent module trap (see Figure 2), and sampling was conducted for 8.5 hours at a nominal rate of 10 cfm. Applying a correction factor for the PCP detected in the control resin, the concentration of PCP detected in the air sample was approximately 160 pg/dscf, or .05 ppt.

While these data are suggestive of the presence of PCP and possible other isomers in the combustion air for the incinerator, a far more detailed study would be required to determine any relationship between these data and emissions of dioxins.

Waste Oil and Fuel Oil Samples

Samples of waste oil and fuel oil collected at Facility B were subjected to analysis for tetrachlorodibenzo-p-dioxins and tetrachlorodibenzofurans. Procedures for this work are included in Appendix C. Table 13 presents the results of capillary column GC/HRMS analysis of these samples. No detectable levels of TCDD or TCDF were found in either waste oil or fuel oil samples.

TABLE 13. CAPILLARY GC/HRMS ANALYSIS OF WASTE OIL SAMPLES FOR TCDD AND TCDF

Sample code	Weight (g)	Fortification* level (ng)	Concentration of TCDD (ppt)†	Detection limit (ppt)	Concentration of TCDF (ppt)	Detection limit (ppt)	Percent recovery
Waste oil	1.0	3.5	nd§	330	nd	620	85
Fuel oil	1.0	3.5	nd	110	nd	160	80

* Samples were fortified with the internal standard ^{13}C-2,3,7,8-TCDD.
† Parts per trillion.
§ None detected.

The absence of TCDD and TCDF from these samples indicates that the detection of these compounds in flue gas samples did not result from incomplete combustion of preexisting TCDDs or TCDFs in the fuel. On the other hand, these data do not preclude the possibility of precursors in the waste oil and/or fuel oil leading to formation of TCDDs and TCDFs in the combustion process. Clearly, further study would be required to test this hypothesis.

ESP Ash Samples

Table 14 summarizes the results of packed column GC/HRMS analysis of ESP ash samples from Facility C. It is apparent that TCDD and TCDF concentrations found in ESP ash collected during the dRDF burn were higher than in that collected during the coal burn test. The significance of this finding is discussed in Section 5 of this report.

TABLE 14. ANALYSIS OF ESP ASH SAMPLES FROM FACILITY C*

Fuel burned	Total TCDD (ppt)	Maximum 2,3,7,8-TCDD (ppt)	Total TCDF (ppt)	Maximum 2,3,7,8-TCDF (ppt)
dRDF	7,300	2,000	154,100	42,700
Coal	600	200	12,300	4,300

* Samples processed by Soxhlet extraction.

SECTION 4

DISPERSION MODELING

INTRODUCTION

The results of the TCDD analyses conducted in this program were used to predict maximum expected ground level concentrations through the application of computer dispersion modeling techniques. The program used was PTMAX, one of six dispersion modeling programs made available through the U.S. EPA in the Users Network for Applied Modeling of Air Pollution (UNAMAP) series.[8,10]

PTMAX assumes that a steady-state Gaussian plume model is applicable to determining ground level concentrations. Concentrations are determined as a function of wind speed and stability. Six atmospheric stability classes are analyzed by PTMAX, ranging from Class 1 (most unstable) to Class 6 (most stable). The results of PTMAX can be used to identify the combination of wind speed and stability class that produces the maximum 1-hour concentration of a given pollutant at ground level.

PTMAX has been employed by others to characterize the ground level concentrations of pollutants emitted by waste burning facilities.[7] This program is generally recognized as a useful tool for initial analysis of the impact of stationary source pollution sources on their surrounding environment. It must be cautioned, however, that PTMAX assumes a relatively uniform terrain and is not applicable when aerodynamic downwash affects the plume emitted from the Stack.[8,10]

PTMAX INPUT DATA

The input data required by PTMAX consists of the ambient air temperature, physical stack height, stack gas temperature, stack gas volume flow rate, and pollutant emission rates (source strength). Table 15 summarizes the input data for the PTMAX analyses conducted in this program. An ambient temperature of 20°C (273°K) was assumed for all analyses. The stack heights at each facility were taken from available engineering drawings. Stack temperatures represent the average of measurements taken during the sampling periods. Stack volume flow rates were determined as a theoretical gas flow rate based on the fuel ultimate analyses and measured stack gas composition data (see Section 2). The source strengths reported on Table 15 represent the concentrations of total TCDD and maximum 2,3,7,8-TCDD as determined by packed column GC/HRMS (see Section 3).

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TABLE 15. PTMAX INPUT DATA

Facility	Date	Ambient air temp. (°K)	Stack height (M)	Stack temp. (°K)	Stack flow rate (DSCM/sec)	Source strength (g/sec) TCDD	Source strength (g/sec) Max 2,3,7,8-TCDF
A	09-16-80	293	10	475	5.598	4.7×10^{-8}	2.0×10^{-8}
	09-18-80	293	10	474	5.588	6.0×10^{-9}	1.6×10^{-9}
	10-22-80	293	10	481	6.664	9.0×10^{-9}	2.0×10^{-9}
	10-23-80	293	10	467	6.664	9.6×10^{-9}	2.0×10^{-9}
B	12-08-80	293	23	492	4.018	1.8×10^{-8}	1.1×10^{-8}
	12-09-80	293	23	496	3.620	1.4×10^{-8}	4.2×10^{-9}
	12-10-80	293	23	499	3.579	8.9×10^{-9}	3.8×10^{-9}
C	04-01-81	293	27	412	6.963	2.1×10^{-7}	6.7×10^{-8}
	04-07-81	293	27	417	8.092	2.4×10^{-7}	6.9×10^{-8}

PTMAX RESULTS

Table 16 summarizes the results of the PTMAX analyses. The maximum 1-hr ground level concentrations are shown for total TCDD and maximum 2,3,7,8-TCDD. Also indicated on this table are the stability classes, wind speeds, plume heights, and distances of the maximum concentrations from the sources.

No significant differences exist at a 95 percent confidence level (Student's t-test, variances not assumed equal) between the ground level concentrations predicted for Facility A and Facility B. Although the concentrations for total TCDD and maximum 2,3,7,8-TCDD at Facility C appear to be 10 and 100 times greater than those reported for Facilities A and B, more samples would be required to statistically verify this observation.

The results of the PTMAX analyses can be used to determine an average dilution factor which when multiplied by the source strength in g/sec will approximate the maximum ground level concentration. The average dilution factors computed for Facility A, B, and C are 3.7×10^{-5}, 2.2×10^{-5}, and 1.5×10^{-5}. In general, an approximate maximum ground level concentration can be determined by multiplying the source strength by 10^{-5}.

TABLE 16. PTMAX RESULTS

Facility	Date	Maximum ground level concentration (g/m^3)	Stability class	Wind Speed (m/sec)	Plume height (m)	Distance of maximum concentration (km)
TCDD RESULTS						
A	09-16-80	1.94×10^{-12}	3	10	18.9	.189
	09-18-80	2.34×10^{-13}	3	10	18.9	.189
	10-22-80	3.03×10^{-13}	3	10	20.3	.204
	10-23-80	3.35×10^{-13}	3	10	20.0	.200
B	12-08-80	3.89×10^{-13}	1	2	59.2	.287
	12-09-80	3.25×10^{-13}	1	2	56.8	.277
	12-10-80	2.07×10^{-13}	1	2	56.7	.277
C	04-01-81	3.47×10^{-12}	1	2	69.5	.330
	04-07-81	3.44×10^{-12}	1	2.5	65.9	.315
MAXIMUM 2,3,7,8-TCDD RESULTS						
A	09-16-80	7.78×10^{-13}	3	10	18.9	.189
	09-18-80	6.25×10^{-14}	3	10	18.9	.189
	10-22-80	6.74×10^{-14}	3	10	20.3	.204
	10-23-80	6.99×10^{-14}	3	10	20.0	.200
B	12-08-80	2.38×10^{-13}	1	2	59.2	.287
	12-09-80	9.75×10^{-14}	1	2	56.8	.277
	12-10-80	8.84×10^{-14}	1	2	56.7	.277
C	04-01-81	1.11×10^{-12}	1	2	69.5	.330
	04-07-81	9.99×10^{-13}	1	2.5	65.9	.315

SECTION 5

CONCLUSIONS

INTRODUCTION

This program focused on the collection of four major areas of data at three municipal refuse combustion facilities: TCDD and TCDF concentrations in stack gas samples, combustion air samples, and selected process stream samples; and dispersion modeling of maximum ground level concentrations of TCDDs. The principal conclusions resulting from this program consist of the following.

STACK EMISSIONS

Quality Control

The validity of stack gas samples collected in this program was established by adherence to strict trace organic sampling procedures, outlined in Appendix A. In addition, sampling method blanks and extensive analytical controls were analyzed in conjunction with the actual stack samples. The results of these analyses indicated that no significant portion of the amounts of TCDDs and TCDFs detected in stack samples could be attributed to the sampling procedures or sampling trains. Even though the Modified Method 5 blank at Facility B showed significant levels of TCDDs, the stack data were not rejected because other blanks taken at this facility did not show contamination. The results of the analytical controls detailed in Appendix C substantiate the validity of the stack gas samples. Since the background levels of TCDDs and TCDFs were extremely low in comparison to stack samples, no corrections of the stack samples for background concentrations were made.

TCDD and TCDF Stack Emissions

The emission rates of TCDDs determined from stack samples taken in this program ranged from 6.0×10^{-9} g/sec to 238×10^{-9} g/sec (1.4×10^{-5} g/ton fuel fired to 63×10^{-5} g/ton fuel fired). The emission rates of TCDFs determined from stack samples ranged from 16×10^{-9} g/sec to 2170×10^{-9} g/sec (5.0×10^{-5} g/ton fuel fired to 530×10^{-5} g/ton fuel fired). The amounts of TCDF emitted ranged from approximately 2 to 10 times higher than the amounts of TCDD emitted on g/ton and g/sec basis.

There was no significant difference between the emissions of TCDDs from Facilities A and B. Emissions of TCDFs also did not differ significantly between Facilities A and B. Although the data from Facility C seem to indicate higher emission rates than at the other two facilities, insufficient samples were taken to statistically substantiate this conclusion.

The data derived from the testing at Facility A indicated that there was no significant difference between TCDD and TCDF emissions during the burning of as-received or of trommeled refuse. The data obtained during testing at Facility B suggested that there was a positive relationship between the emission rates of TCDFs and TCDDs and the feed rate of waste oil burned during the tests. Figure 10 illustrates the TCDF data obtained during the testing

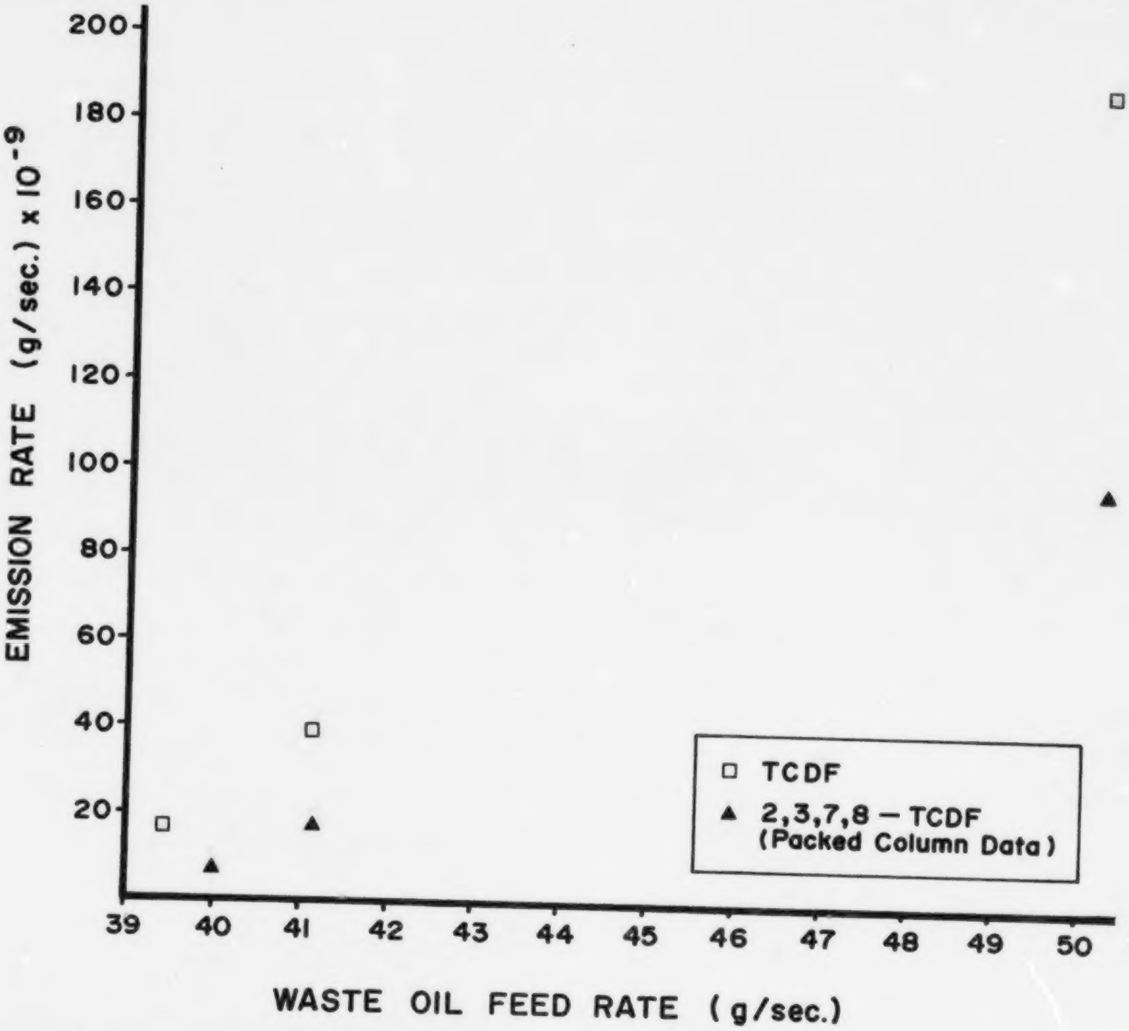

Figure 10. TCDF emission rates as a function of waste oil feed rates at Facility B.

conducted at Facility B as a function of the waste oil feed rate. Figure 11 illustrates the TCDD data as a function of the waste oil feed rate. Although these data are far from conclusive, they do strongly suggest the need for further study of TCDF and TCDD emissions from the combustion of waste oils.

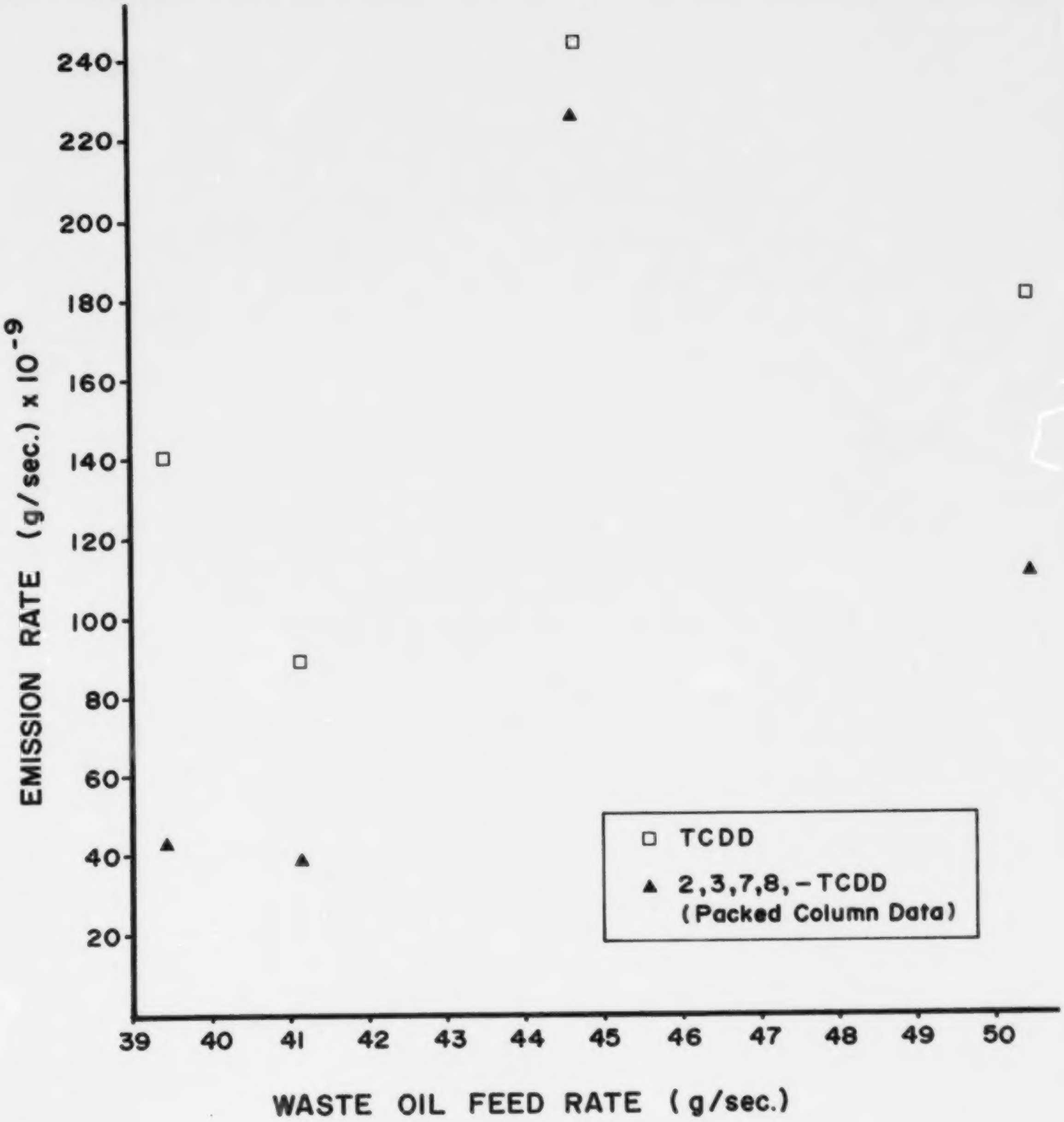

Figure 11. TCDD emission rates as a function of waste oil feed rates at Facility B.

The results of the analysis of stack gas samples from Facility C indicated that nearly equal amounts of TCDDs and TCDFs were emitted during the combustion of dRDF and during the combustion of coal. Since the analysis of method and analytical blanks in conjunction with these stack samples showed no detectable amounts of TCDDs or TCDFs, there is no immediate reason to doubt the validity of the stack sample data. However, it should be noted that only one sample was taken during each of the firing modes. The statistical confidence of these data is therefore low. Nevertheless, these data suggest the need for further study of the emissions of TCDDs and TCDFs from coal combustion. Previous studies have not conclusively established whether TCDDs in particular are emitted from coal combustion.

TCDD and TCDF Isomer Analysis

The data obtained on TCDD and TCDF isomer composition of stack gas samples showed that the maximum amounts of TCDDs and TCDFs identified by packed column chromatography as the 2,3,7,8 isomers and coelutors averaged 41 and 44 percent, respectively. The amounts confirmed as 2,3,7,8 isomers by capillary column GC/HRMS were considerably lower, at 13 percent for TCDD and 24 percent for TCDF. In general, it appears that employing packed column GC/HRMS analysis for the identification of 2,3,7,8 isomers provides a useful "worst case" assessment of the amounts of these isomers actually present. The data presented in Appendix C of this report also show that nearly all the 22 TCDD isomers and many of the TCDF isomers were routinely detected at nearly equal concentrations in samples analyzed by capillary column GC/HRMS.

COMBUSTION AIR SAMPLES

The general conclusions reached from the analysis of combustion air samples from Facilities B and C indicated that in some cases trace amounts of TCDDs and TCDFs were detected. These amounts were, at most, several orders of magnitude less than those found in comparable stack samples. Since the sampling methods employed did not prevent the inclusion of downwash flue gas into these samples, the TCDDs and TCDFs detected may represent diluted flue gases rather than ambient air at the facilities.

OTHER SAMPLES

Resin Samples

The results of the pentachlorophenol (PCP) analysis of the combustion air sample taken at Facility A suggest a possible origin for at least part of the TCDDs detected in stack gas samples. Previous studies have implicated chlorinated phenols as precursors for chlorodioxin formation by thermal decomposition.[11] This mechanism may have been involved in the emission of TCDDs from the incineration process. Clearly, more study would be required to test this hypothesis.

Waste Oil and Fuel Oil

The results of TCDD and TCDF analysis of waste oil and fuel oil from Facility B indicated no detectable levels of these compounds. This result does not, however, rule out the possibility of other unidentified compounds acting as precursors for TCDD and TCDF formation. The relationship between waste oil substitution rate and emissions suggests the need for further study of waste oil burning emissions.

Electrostatic Precipitator (ESP) Ash Samples

The samples of ESP ash taken at Facility C showed far greater concentrations of TCDDs and TCDFs during the dRDF burning test period than the coal test period. Since an interim period of only 3 days elapsed between the end of dRDF burning and the collection of the coal firing sample, a possible explanation for the presence of TCDDs in the coal firing period sample can be hypothesized. Tetrachlorodibenzo-p-dioxins may have been entrained on the particulate trapped in the ESP during dRDF combustion. Still present during the coal combustion test, they could then have been eluted into the stack samples. This hypothesis could be resolved only by the performance of more in-depth sampling at the facility after prolonged combustion of coal only, following a thorough cleaning of the ESP.

DISPERSION MODELING

The results of the PTMAX dispersion modeling of TCDD emissions from the three test facilities indicated maximum ground level concentrations on the order of 10^{-13} to 10^{-12} g/m^3. The analysis of packed column data for 2,3,7,8 TCDD and coelutors indicated maximum ground level concentrations from 10^{-14} to 10^{-12} g/m^3. Maximum ground level concentrations of TCDDs averaged approximately four to five orders of magnitude less than concentrations detected in stack gas samples.

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APPENDIX A

STACK SAMPLING METHODS

MODIFIED METHOD 5 TRAIN

Because of the complexity of operating and recovering sample from the Modified Method 5 train, a detailed procedures manual has been developed to facilitate field use of this train. This manual includes sections describing pretest preparations, recovery procedures, sample handling and storage, and laboratory facilities.

PRETEST PREPARATIONS

The preparation of glassware, filters, glass wool, aluminum foil, and XAD-2 resin is completed prior to departure for the test site. The procedures for the various preparations are as follows.

Glassware Preparation

Each piece of glassware which is in contact with the sample is cleaned according to the following procedure:

1. Wipe off all adhering materials
2. Wash with soap and water
3. Completely submerse in chromic acid for a minimum of 6 hours. This allows two batches to be cycled during a normal 8-hr work day.
4. Thoroughly rinse with tap water
5. Rinse with distilled H_2O
6. Rinse with solvent
7. Seal exposed ends with clean (solvent scrubbed) aluminum foil.

This procedure is performed prior to each new test location or between specific test conditions.

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Aluminum Foil Preparation

Aluminum foil is used to cap openings of the glassware after cleaning and during several stages of the recovery process. Because the foil is used to prevent entry of potential contaminants, it must be solvent washed.

1. One side of the foil is wiped with a Kimwipe and solvent. It has been found that a large Kimwipe, folded and held with the sponge clamps, provides adequate scrubbing action. As the Kimwipe gets dirty, it can be refolded or replaced. The sponge clamps eliminate contamination from solvent contact with the persons hands.
2. After scrubbing, the foil is held with the clamps or forceps and rinsed with solvent.
3. The foil is then folded, cleaned sides together, and stored in either a clean sample jar or wrapped in a large piece of clean foil.

Various sized pieces of foil are required throughout the recovery procedure. Cutting several pieces into approximate 2- to 3-in. squares prior to use may be helpful in respect to recovery time. Large pieces of clean foil are required to protect each clean filter.

Filter Preparation

Prior to use, all Modified Method 5 particulate filters are solvent rinsed by the following procedures:

1. Set up a vacuum filtration system using a clean 1-ℓ flask and 10-in. funnel. The filter frit and gasket are set in the funnel. This serves as a support for the filters.
2. Up to 25 filters are cleaned at one time using 1 liter of solvent. The top and bottom 3 filters are discarded.
3. As soon as all the solvent has passed through, the vacuum is shut off. This reduces the amount of "lab air" drawn through the filters and the potential contaminants it carries.
4. Each cleaned filter is then sealed in a clean piece of aluminum foil.

Glass Wool Preparation

Glass wool is used to plug the resin chamber section of the sorbent trap. As it is in direct contact with the sample, the glass wool must be thoroughly cleaned.

1. Depending on the number of test runs, cut a sufficient quantity of glass wool and place in a cleaned sample jar. A 500-cc jar is usually sufficient.

2. Extract the glass wool three times with 300- to 400-cc portions of $CH_3OH:CH_2Cl_2$ (1:1). (The volume of solvent should be adjusted accordingly with the quantity of glass wool.)

3. The glass wool may then be stored in the sample jar until needed.

Resin Preparation

For each test, approximately 45 grams of XAD-2 sorbent resin is used. Prior to use it is prepared according to prescribed EPA Level 1 procedures.

ASSEMBLY/LEAK CHECK

The general configuration of the Modified Method 5 train is essentially the same as the Standard Method 5 train. The variations in assembly are as follows:

1. Vacuum grease may not be used on any surface which has sample contact. This includes the surfaces between the probe nozzle and the outlet of the No. 3 impinger.

   Wide Teflon tape is stretched over the spherical member of the joint to obtain leak-free seals. This method results in a thin smooth Teflon layer which seals quite well. A hole is cut in the center of the stretched Teflon with a solvent rinsed razor blade.

2. The sorbent trap is situated between the filter assembly outlet and the first impinger. A cylindrical support has been constructed to hold the sorbent trap in a vertical position on the back side of the oven section of the sample box. It is positioned condenser section down, resin chamber up. Teflon tubing with appropriate hose adaptors is used to make the connection from the filter outlet to the condenser inlet and from the resin chamber outlet to the impinger No. 1 inlet.

3. The arrangement of the impingers and their respective solutions are as follows:

No. 1 - Greenburg-Smith	100 mℓ HPLC H_2O
No. 2 - Modified Greenburg-Smith	empty
No. 3 - Modified Greenburg-Smith	empty
No. 4 - Modified Greenburg-Smith	Silica gel - full capacity

4. The particulate filter is not preweighed.

RECOVERY OF THE ORGANIC SAMPLE FROM MODIFIED METHOD 5 SAMPLE TRAIN

Philosophy of Sample Recovery

Recovery of the Modified Method 5 sample should be accomplished with minimal exposure of sample and sample contact surfaces to potential contaminants. Contamination may result from excessive exposure to the laboratory atmosphere, improper handling, or the use of improperly cleaned equipment. The primary methods of reducing potential contamination are:

1. Disassembling one train component at a time.
2. Immediately capping exposed sample contact areas with solvent rinsed aluminum foil.
3. Wearing two pairs of gloves (nylon over cotton) while recovering sample.
4. Solvent rinsing all tools (tweezers, spatulas, scissors, etc.) immediately prior to each use.

For the purpose of this test, it is felt that the recovery of an uncontaminated sample is more important than the complete recovery of all material trapped by the train. For example, if silica gel is found in the No. 3 impinger, it is better to eliminate recovery of the No. 3 impinger than to contaminate the impinger sample with silica gel. A notation in the log book would then be made explaining the circumstances requiring this procedure change. This philosophy is what separates the recovery procedure from cleaning. Recovery includes reclaiming only that part of the sample which will wash out through repeated solvent rinses. For example, the Standard Method 5 procedure for recovering the sample from the probe requires that the probe be washed and brushed. The recovery of sample from the MM5 probe requires only a solvent rinse. After the solvent rinse is completed and the sample properly stored, the probe may then be "cleaned" by brushing.

For notation of various operating and recovery conditions, a log book is maintained. Daily entries are made by the stack and recovery teams. Figure A-1 is a summary sheet of data pertinent to normal MM5 sampling and recovery work. Besides that information, the log book is used to note any unusual circumstances which may occur during operation or sample recovery.

Sample Recovery Procedures

A schematic of the recovery procedures is indicated in Figure A-2.

Sample 3-P--

Particulate sample (3-P) includes rinses from:

- probe nozzle
- probe
- cyclone bypass

Date:

Location:

Fuel type:

Sample volume:

Combustion resin system ______ or MM5 ______

Leak Check

Laboratory

Rate: __________ CFM

Initial meter reading: ________ CF

Final meter reading: ________ CF

Field

Rate: __________ CFM

Initial meter: ________ CF

Final meter: __________ CF

Solvent used in recovery of:

MM5

3 - I - A ______
3 - XR - A ______
3 - P - A ______

Subtotal ______

3 - I - B ______
3 - XR - B ______
3 - P - B ______

Subtotal ______

TOTAL ______

Figure A-1. MM5 organic stack sampling: daily summary.

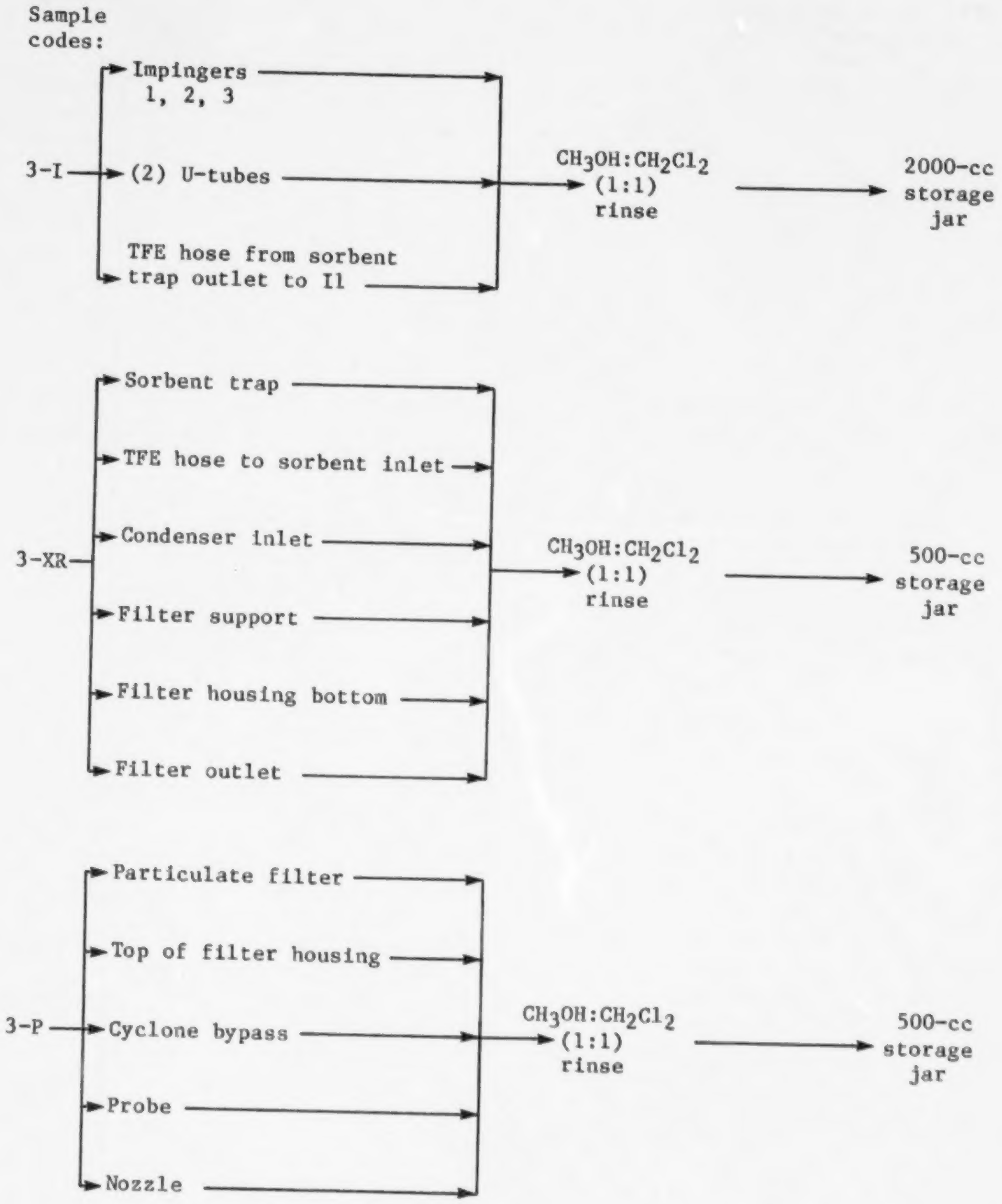
Sample codes:
Impingers 1, 2, 3
3-I
(2) U-tubes
TFE hose from sorbent trap outlet to I1
$CH_3OH:CH_2Cl_2$ (1:1) rinse
2000-cc storage jar
Sorbent trap
TFE hose to sorbent inlet
Condenser inlet
3-XR
Filter support
Filter housing bottom
Filter outlet
$CH_3OH:CH_2Cl_2$ (1:1) rinse
500-cc storage jar
Particulate filter
Top of filter housing
3-P
Cyclone bypass
Probe
Nozzle
$CH_3OH:CH_2Cl_2$ (1:1) rinse
500-cc storage jar

Figure A-2. Modified Method 5 sample recovery.

- upper half of filter housing
- particulate filter

Procedure--Weigh in solvent wash bottle. Remove the probe nozzle from the probe and cap the exposed end of the probe with clean aluminum foil.

Nozzle--Rinse the interior surfaces of the nozzle with solvent being careful not to rinse over the exterior surfaces. It is suggested that solvent be introduced through both ends of the nozzle to ensure adequate rinsing of all interior surfaces. Recap the ends of the nozzle with clean aluminum foil.

Probe (requires 2 people)--Hold the outlet end of the probe over the sample recovery funnel and elevate the nozzle end slightly. Introduce a stream of solvent into the nozzle end while rotating the probe slowly. Continue to rotate through three to four rotations while rinsing with approximately 100 to 200 cc of solvent.

(Note: The probe interior is NOT brushed as in the Standard Method 5 procedure. Recap ends with clean aluminum foil.)

Cyclone Bypass--Remove cyclone bypass and cap upper half of filter housing with clean aluminum foil. Introduce approximately 10 to 20 cc of solvent into the cyclone bypass and rotate and agitate to contact all interior surfaces. Repeat this procedure three times.

Filter and Upper Half of Housing (2 people)--Disconnect and disassemble the filter housing and with cleaned tweezers and spatula carefully fold the particulate filter inward until it will fit into the sample bottle easily. Set aside the lower half of the filter housing and the frit in the clean area. Rinse the interior of the upper half of the filter housing by directing the solvent stream near the edge of the bell and rinsing down and out the neck. Care should be taken not to get too near the lip and contaminate the sample by washing down the exterior of the bell. Rinse around the bell three times. Set aside in clean area on clean aluminum foil.

Rinse down the sample recovery funnel and cap the sample bottle.

Reweigh the solvent wash bottle.

Sample 3-XR--
Resin sample (3-XR) bottle contains rinses from:

- filter frit
- lower half of filter housing
- U-connector
- modified impinger inlet connector
- TFE connecting tube
- resin trap/condenser

Frit--Pick up the frit with cleaned tweezers and carefully remove TFE tape from around edges. Discard tape. Rinse frit into sample recovery funnel. Rinse with approximately 50 cc of solvent. Set frit aside in clean area on clean aluminum foil.

Lower Half Filter Housing--Rinse in same manner as upper half and set aside in clean area on clean aluminum foil.

U-tube Connector--Disconnect and rinse by partially filling with solvent (10 to 20 cc), rotating and rocking to ensure solvent contact on all interior surfaces. Repeat three times.

Oven Outlet Connector--Rinse the interior surfaces of the connector with solvent. To ensure complete rinsing it will be necessary to introduce the solvent from both ends of the piece. Use approximately 50 cc of solvent.

TFE Connectors--Disconnect and rinse three times with approximately 10 to 20 cc of solvent using a rocking motion to ensure contact with all inner surfaces.

Resin Trap/Condenser--Remove the glass wool plug from the end of the resin chamber with solvent rinsed tweezers and place it directly into the sample container, being careful not to lose any of the resin.

Invert the resin trap over the sample recovery funnel and rinse through the condenser, the frit, and out the resin chamber into the sample container. The condenser section of the trap should be filled with solvent with a vigorous spraying action and then allowed to drain through the frit and resin chamber approximately four to five times. Use 200 to 300 cc of solvent.

Set the condenser aside in the clean area and allow to dry.

Rinse down funnel and close sample bottle.

Reweigh solvent squirt bottle.

Sample 3-I--
Impinger sample bottle (3-I-1,2,3,) contains rinses and condensate from:

- resin trap outlet connector
- impinger No. 1
- U-tube connector
- impinger No. 2
- U-tube connector
- impinger No. 3

Weigh solvent squirt bottle.

As U-tubes are disconnected, they can be taken directly to sample recovery hood and rinsed three times with approximately 5 to 10 cc of the solvent mixture.

Disconnected impingers are immediately capped off with clean aluminum foil, weighed to determine weight gain, and placed in the sample recovery hood.

Without disconnecting the impinger stem from the bottom, pour out the impinger contents through the side arm into the sample bottle. Rinse three times with 20- to 30-cc portions of solvent by squirting the solvent down the center tube into the impinger. Agitate the solvent so that it splashes over the outer surface of the inner tube and completely rinse over the inner surfaces of the impinger bottom. Pour the solvent rinses out through the side arm and into the sample bottle. The impingers can now be recapped until train is reassembled for the next run.

Rinse down funnel with solvent into sample bottle. Weigh squirt bottle.

SAMPLE HANDLING

As charted in Figure A-2, samples are stored in either 500- or 2000-cc storage jars. Each jar is labeled with the appropriate sample code, site location, date, recovery time, and initials of recovery team members.* The volume level of the sample is then marked on the storage jar. To protect the samples from photochemical degradation, each sample jar is completely wrapped in aluminum foil. This foil does not have to be solvent cleaned. After wrapping, the storage jar is relabeled, as before. A tamper-proof seal is then applied to each bottle to assure sample integrity during transport.

LAB REQUIREMENTS

General physical requirements for the lab include:

- explosion proof hood - 4 to 6 ft wide
- laminar flow hood - hepa filtered air
- 6 to 12 ft of bench top work area

Ideally, the lab should be a positive pressure clean room environment, free from any sources of volatile or particulate organics.

All sample recovery work is done under the hood. The work area of the hood should be cleaned and covered with clean room sheeting. Various types of support equipment are used to aid in sample recovery. These include:

- Stainless steel tray to serve as a solvent catch basin when rinsing items not included in the sample recovery scheme.

- A ring stand and a large ring to support the funnel over the sample jar.

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* Each leg of the Modified Method 5 is identified by either an A or B at the end of the label information. Sample blanks are identified by the word BLANK following the label sequence on the sample log only (see Appendix E).

- Two Teflon wash bottles - one which contains a known mass of solvent and is used exclusively for sample recovery and another one used for various solvent rinses outside the sample recovery scheme.

- Clean foil to rest glassware on during recovery procedure.

- Tweezers, spatula, sponge clamp, etc.

The workbench surface is also wiped down with solvent and covered with clean room sheeting.

SOURCE ASSESSMENT SAMPLING SYSTEM TRAIN

Because of the complexity of operating and recovering sample from the Source Assessment Sampling System (SASS) train, a detailed procedures manual has been developed to facilitate field use of this train. This manual includes sections describing pretest preparations, recovery procedures, sample handling and storage, and laboratory facilities.

PRETEST PREPARATIONS

The preparation of glassware, filters, aluminum foil, and the SASS train components is completed prior to departure for the test site. The procedures for the various preparations are as follows:

Aluminum Foil Preparation

Aluminum foil is used to cap openings of the glassware after cleaning and during several stages of the recovery process. Because the foil is used to prevent entry of potential contaminants, it must be solvent washed.

1. One side of the foil is wiped with a Kimwipe and solvent. It has been found that a large Kimwipe, folded and held with the sponge clamps, provides adequate scrubbing action. As the Kimwipe gets dirty, it can be refolded or replaced. The sponge clamps eliminate contamination from solvent contact with the persons hands.

2. After scrubbing, the foil is held with the clamps or forceps and rinsed with solvent.

3. The foil is then folded, cleaned sides together, and stored in either a clean sample jar or wrapped in a large piece of clean foil.

Various sized pieces of foil are required throughout the recovery procedure. Cutting several pieces into approximate 2- to 3-in. squares prior to use may be helpful in respect to recovery time. Large pieces of clean foil are required to protect each clean filter.

Filter Preparation

Prior to use, all SASS particulate filters are solvent rinsed by the following procedures:

1. Set up a vacuum filtration system using a clean 1-ℓ flask and 10-in. funnel. The filter frit and gasket are set in the funnel. This serves as a support for the filters.

2. Up to 25 filters are cleaned at one time using 1 liter of solvent. The top and bottom 3 filters are discarded.

3. As soon as all the solvent has passed through, the vacuum is shut off. This reduces the amount of "lab air" drawn through the filters and the potential contaminants it carries.

4. Each cleaned filter is then sealed in a clean piece of aluminum foil.

Resin

For each test approximately 150 grams of XAD-2 sorbent resin is used. Prior to use it is prepared according to prescribed EPA Level 1 procedures

Cheesecloth

Cheesecloth is used for sample recovery from the organic module condenser unit. The cheesecloth is prepared according to the following procedures:

1. Cut several pieces of cheesecloth into approximate 4-in. squares. The quantity is dependent upon the number of tests - assume 2 pieces per test.

2. Place the pieces into a clean 2000-cc storage jar.

3. Extract the cheesecloth three times by shaking it in the container with 1 liter of solvent (1:1, $CH_3OH:CH_2Cl_2$). The volume of solvent and storage jar may be adjusted accordingly with the amount of cheesecloth being extracted.

4. After extraction, the solvent is decanted off and the cheesecloth is stored in the storage jar until needed.

SASS Train Passivation*

All metal and glass surfaces in the sampling train that come in contact with the sample are passivated by a 30-min standing contact with 15 percent volume for volume (v/v) aqueous nitric acid. A stiff nylon brush or hard Teflon scraper is used to aid in cleaning encrusted materials from the surfaces if necessary. The parts are initially agitated to remove trapped air bubbles, rinsed with tap H_2O, and then rinsed with distilled water. They are then rerinsed by spraying thoroughly with solvent (1:1, $CH_3OH:CH_2Cl_2$) (taking care of all surfaces) and allowed to dry.

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* This section is adapted from IERL/RTP Procedures Manual:Level 1 Environmental Assessment, 2d ed., EPA Publication No. 600/F-78-201.

Passivation should be carried out initially (as stated above) and then every 6 months when the frequency of tests is one per month or less, and monthly for testing in excess of one per week. If the tests are more frequent or of longer duration, passivation should be conducted more frequently. If corrosion has occurred, the corrosion should be removed and the passivation repeated. The passivation and rinse solutions should be replaced after every fourth use or should be discarded weekly.

Storage Jars

For each SASS train run, three 2000-cc and five 500-cc glass storage jars with Teflon lined lids are used. Each jar is cleaned prior to use according to the following procedure:

1. Fill sample containers with concentrated chromic acid solution and soak overnight.
2. Rinse containers thoroughly with distilled water.
3. Rinse containers three times with HPLC grade water.
4. Rinse containers three times with $CH_2Cl_2:CH_3OH$ (1:1).
5. Place Teflon lined lids (previously cleaned with (1:1 $CH_2Cl_2:CH_3OH$) on cooled containers and store in shipping containers.

NOTE: All solvents are of distilled in-glass grade (nanograde) or better.

Reagents

For each SASS train run, the following quantities of reagents are used:

3 liters of solvent (1:1, $CH_3OH:CH_2Cl_2$)

1 liter of HPLC H_2O

150 grams of XAD-2 sorbent resin

2.5 kg of 3 to 8 mesh indicating silica gel

Assembly/Leak Check

The Acurex Corporation/Aerotherm Division Source Assessment Sampling System Operating and Service Manual provides a detailed description for set up and leak checking the SASS train. The following procedures are adaptations to accommodate the special precautions required for trace organic sampling.

Before each component is assembled, it is thoroughly rinsed with solvent. Gloves should be worn when handling sample surfaces of the various components. The train is completely assembled and leak checked in the laboratory. For transportation to the stack, the train is disassembled into four units: (1) the filter/cyclone assembly, (2) the organic module with both stainless steel (SS) braided hoses attached, (3) the impingers, and (4) the probe and nozzle. All openings are capped with clean aluminum foil. Transporting the train in this manner reduces handling of the various components on the stack, reduces the potential of contamination, and facilitates leak checking on the stack.

Table A-1 lists the tools necessary for SASS train assembly. The following components are wrapped with Teflon tape to aid in leak checking and disassembly.

- The lip of each cyclone collection cup.
- The threads on the No. 3 cyclone.
- Tape around the circumference of either the front or back half of the filter housing beyond the area where the O-ring is seated. This aids in separating the filter housing after sampling.

TABLE A-1. TOOL REQUIREMENT FOR SASS TRAIN

Wrenches	Screw drivers
(1) 3/8 in. to 7/16 in.	1/8 in. slot
(2) 3/4 in. to 7/8 in.	3/8 in. slot
(1) 5/8 in. to 9/16 in.	No. 0 Phillips
(2) 1 1/8 in. to 1 1/16 in.	No. 2 Phillips
(1) 1 3/8 in. to 1 7/16 in.	
(1) 1 in.	Miscellaneous
(1) 13/16 in.	
(1) 11/16 in.	3/8 in. nut driver
(1) 1/2 in.	Combination pliers
(1) 5/8 in., long handle	Hex key set

To facilitate the leak check, the following procedures are employed.

1. To obtain leak-tight seals, several of the O-rings and gaskets require periodic replacement. Table A-2 is the recommended replacement schedule.

TABLE A-2. SASS TRAIN, O-RING/GASKET INVENTORY/REPLACEMENT SCHEDULE

Date ____________________

	Replacement schedule		
	After passivation	Per run	As required by: visual inspection or leak check
Impinger			
Cap (175-306911-02-2-234V)	X		
Fitting seal (175-307125-2-116B)			X
Filter assembly (175-306910-03-2-162V)	X	X	
Organic module			
5 1/2 in. (175-300082-02-1-161V)	X		X
5 1/4 in. (175-300084-03-2-160V)	X		X
3 3/4 in. (175-300083-02-2-154V)	X		X
Gasket (7233-079-1)			X
Cyclones			
No. 1. 6 1/2-in. cap (175-300207-01-2-160V)	X		X
4-in. collection bowl seal (7079-217-02)	X	X	
No. 2. 3 1/2-in. cap (175-300262-01-2-153V)	X	X	
4-in. collection bowl seal (7079-217-02)	X	X	
No. 3 Upper slip ring (1 3/8 in. × 1 3/4 in. × 1/16 in.) (7233-040-02)	X		X
Lower slip ring (1.18 in. × 1 3/4 in. × 1/16 in.) (7233-033-04)	X		X
Upper cap gasket (1.43 in. × 1.63 in. × 1/16 in.) (175-300071-02)	X		X
Collection bowl seal (1.09 in. × 1.63 in. × 1/16 in.) (7233-033-03)	X		X

2. The organic module tends to be a major leak source. To rectify this, Teflon tape is used in four areas, around the top flange of the sorbent trap and around the three outer seals prior to putting on the ring clamps.

RECOVERY OF THE ORGANIC SAMPLE FROM SASS TRAIN

Philosophy of Sample Recovery

Recovery of the SASS sample should be accomplished with minimal exposure of sample and sample contact surfaces to potential contaminants. Contamination may result from excessive exposure to the laboratory atmosphere, improper handling, or the use of improperly cleaned equipment. The primary methods of reducing potential contamination are:

1. Disassembling one train component at a time.
2. Immediately capping exposed sample contact areas with solvent rinsed aluminum foil.
3. Wearing two pairs of gloves (nylon over cotton) while recovering sample.
4. Solvent rinsing all tools (tweezers, spatulas, scissors, etc.) immediately prior to each use.
5. Preliminary cleaning and routine maintenance of laboratory surfaces.

For the purpose of this test, it is felt that the recovery of an uncontaminated sample is more important than the complete recovery of all material collected by the train. For example, if silica gel is found in the No. 3 impinger it is better to eliminate recovery of the No. 3 impinger than to contaminate the impinger sample with silica gel. A notation in the log book would then be made explaining the circumstances requiring this procedure change. This philosophy is what separates the recovery procedure from cleaning. Recovery includes reclaiming only that part of the sample which will wash out through repeated solvent rinses. For example, standard stack sampling procedures for recovering the sample from the probe require that the probe be washed and brushed. The recovery of sample from the SASS probe requires only a solvent rinse. After the solvent rinse is completed and the sample properly stored, the probe may then be "cleaned" by brushing.

For notation of various operating and recovery conditions, a log book is maintained. Daily entries are made by the stack and recovery teams. Figure A-3 is a summary sheet of data pertinent to normal SASS sampling and recovery work. Besides that information, the log book is used to note any unusual circumstances which may occur during operation or sample recovery.

General Recovery Procedures

- Prior to the first rinse and after the final rinse in the recovery of each sample the weight of the solvent wash bottle is recorded.

Date:

Location:

Fuel type:

SASS ________

Sample volume:

Leak Check

Laboratory

Rate: __________ CFM

Initial meter reading:_________CF

Final meter reading: _________CF

Field

Rate: __________CFM

Initial meter: _________CF

Final meter: __________CF

Solvent used in recovery of:

SASS

2I - 1,2,3 ______
2 CD ______
2 XR ______
2 PF ______
2 - 1C ______
2 - 3C ______
2 - 10C ______
2 PR ______
______

TOTAL ______

Figure A-3. SASS organic stack sampling: daily summary.

- As a component is disassembled, it is either rinsed immediately, capped with clean aluminum foil, or set under the laminar flow hood.
- Remove all Teflon tape, gaskets, and O-rings prior to sample recovery and rinsing. These items are removed using clean tools.
- Empty the collected sample into the storage jar prior to rinsing the component.
- Each sample contact surface is rinsed a minimum of three times.
- Care should be taken not to contaminate the sample with washings from the exterior surface of a component.
- Rinse the funnel as the final step before capping the sample jar.
- Reassemble each component as soon as possible and cap exposed openings with clean foil.

(Note: The probe interior is NOT brushed. Recap ends with clean aluminum foil.)

Sample Recovery Procedures

A schematic of the recovery procedures is indicated in Figure A-4.

Sample 2-PR

Contains rinses from

- probe nozzle
- probe

Procedure:

1. Remove the probe nozzle from the probe and cap the exposed end of the probe with clean aluminum foil.
2. Rinse the interior surfaces of the nozzle with solvent being careful not to rinse over the exterior surfaces. It is suggested that solvent be introduced through both ends of the nozzle to ensure adequate rinsing of all interior surfaces. Recap the ends of the nozzle with clean aluminum foil.
3. Hold the outlet end of the probe over the sample recovery funnel and elevate the nozzle end slightly. Introduce a stream of solvent into the nozzle end while rotating the probe slowly. Continue to rotate through three to four rotations while rinsing with approximately 100 to 200 cc of solvent.

Codes:			
2-I·1,2,3,	Impingers 1,2,3, (2) Teflon (TFE) connectors Stainless Steel braided hose (I-1 to organic module)	$CH_3OH:CH_2Cl_2$ rinse	2000-cc storage jar
2-CD	Collected condensate Condensate collection cup	$CH_3OH:CH_2Cl_2$ rinse	2000-cc storage jar
2-XR	Resin Resin trap Organic module Stainless Steel braided hose Back of filter housing Filter frit	$CH_3OH:CH_2Cl_2$ rinse	2000-cc storage jar
2-PF	Particulate filter(s) Front of filter housing Outlet of No. 3 cyclone	$CH_3OH:CH_2Cl_2$ rinse	500-cc storage jar
2-1C	No. 3 cyclone Outlet of No. 2 cyclone	$CH_3OH:CH_2Cl_2$ rinse	500-cc storage jar
2-3C	No. 2 cyclone Outlet of No. 2 cyclone	$CH_3OH:CH_2Cl_2$ rinse	500-cc storage jar
2-10C	No. 1 cyclone	$CH_3OH:CH_2Cl_2$ rinse	500-cc storage jar
2-PR	Probe Probe nozzle	$CH_3OH:CH_2Cl_2$ rinse	500-cc storage jar

Figure A-4. SASS train sample recovery.

Sample 2-10C

Contains sample and rinses from the No. 1 cyclone.

Procedure:

1. Remove the collection cup.
2. Empty contents and rinse three times.
3. Rinse up to the lip, being careful not to get too near the lip and contaminate the sample by washing down the exterior of the cup.
4. Remove the cyclone top (outlet) and set aside.
5. Rinse the cyclone by introducing solvent through the inlet as well as through the top. Rinse a minimum of three times.
6. Approximately 200 mℓ of solvent should be used.

Sample 2-3C

Contains sample and rinses from

- No. 2 cyclone
- Outlet of No. 1 cyclone

Procedure:

1. Rinse the outlet of the No. 1 cyclone by introducing solvent through the outlet stem and then across the inner surface.
2. Recover the sample and rinse the No. 2 cyclone using the procedure outlined for the No. 1 cyclone.
3. The solvent volume should be approximately 250 mℓ.

Sample 2-1C

Contains sample and rinses from

- No. 2 cyclone outlet
- No. 3 cyclone

Procedure:

1. Follow the procedure as outlined for the No. 1 and 2 cyclones.
2. The solvent volume should be approximately 150 mℓ.

Sample 2-PF

Contains sample and rinses from

- No. 3 cyclone outlet
- Filter housing front
- Particulate filter(s)

Procedure:

1. Rinse the No. 3 cyclone outlet as outlined previously.
2. Disassemble the filter housing.
3. Using cleaned tweezers and spatula, carefully fold the particulate filter inward until it will easily fit into the sample jar.
4. Rinse the front half of the filter housing by directing the solvent stream near the edge of the housing and out the inlet.
5. Approximately 150 mℓ of solvent is used.

Sample 2-XR

Contains sample and rinses from

- Filter frit
- Back of filter housing
- SS braided hose
- Organic module
- Resin trap
- Resin

Procedure:

1. Remove the filter frit using clean tweezers or sponge clamps.
2. Hold it over the funnel and thoroughly rinse with solvent from both sides.
3. Rinse the back of the filter housing following the same procedure as for the front half.

4. Rinse out the SS braided hose by introducing solvent alternately from both ends. Rotate and rock the hose to ensure solvent contact on all interior surfaces.

5. Remove the resin trap.

6. Empty the resin into the sample jar and rinse the interior surfaces of the resin trap.

7. Lift out the condenser unit. Place in solvent cleaned SS beaker of appropriate size. Recover rinsing in this beaker.

8. Using the sponge clamps and clean cheesecloth, wipe down the walls of the condenser. This function requires two people; one person wipes while the other adds solvent to the area being recovered.

9. Rinse the inner walls of the organic module into the cleaned SS beaker. If sample appears to be adhered to the walls, wipe it out using clean cheesecloth and sponge clamps.

10. Add all used pieces of cheesecloth to the sample.

11. Approximately 800 mℓ of solvent will be used.

Sample 2-CD

Contains sample and rinses from

- Condensate collect cup
- Teflon hose (from collect cup to jar)
- Collected condensate

Procedure:

1. Use the jar in which the condensate was collected for the sample storage jar.

2. Drain any remaining condensate from the cup to the jar.

3. Determine and record the volume of collected condensate.

4. Leave the TFE drain hose attached to the cup.

5. Rinse the condensate collection cup. Rinse the cup walls only--do not rinse across the flange. Allow enough solvent to rinse the cup as well as the TFE drain hose.

6. Approximately 125 mℓ of solvent will be used.

Sample 2-I-1,2,3

Contains sample and rinses from

- No. 1, 2, and 3 impingers
- Two TFE impinger connections (those which connect the No. 1 and 2 and the No. 2 and 3 impingers)
- SS braided hose

Procedure:

1. Rinse the braided hose as outlined in sample 2-XR.
2. Disconnect and remove the impinger connections.
3. Rinse the connectors by partially filling with solvent (10 to 20 mℓ) and rotating and rocking to ensure solvent contact with all interior surfaces.
4. Record the weight of the impingers.
5. Remove the cap and empty the impinger contents into the sample jar.
6. Do not rinse the interior surface of the cap.
7. Rinse the interior of the impinger stem by introducing solvent through the inlet and then rinse the exterior of the stem.
8. Rinse the impingers by introducing solvent from the top and rotating the impinger to ensure solvent contact with all interior surfaces.
9. Approximately 600 mℓ of solvent is required.

SAMPLE HANDLING

As charted in Figure A-4, samples are stored in either 500- or 2000-cc storage jars. Each jar is labeled with the appropriate sample code, site location, date, recovery time, and initials of recovery team members.* The volume level of the sample is then marked on the storage jar. To protect the samples from photochemical degradation, each sample jar is completely wrapped in aluminum foil. This foil does not have to be solvent cleaned. After wrapping, the storage jar is relabeled, as before. A tamper-proof seal is then applied to each bottle to assure sample integrity during transport.

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* Sample blanks are identified by the word Blank following the label sequence on the sample log only.

LABORATORY REQUIREMENTS

General physical requirements for the laboratory include:

- explosion proof hood - 4- to 6-ft wide
- laminar flow hood - hepa filtered air
- 6 to 12 ft of bench top work area

Ideally, the laboratory should be a positive pressure clean room environment, free from any sources of volatile or particulate organics.

All sample recovery work is done under the hood. The work area of the hood should be cleaned and covered with clean room sheeting. Various types of support equipment are used to aid in sample recovery. These include:

- Stainless steel tray to serve as a solvent catch basin when rinsing items not included in the sample recovery scheme.
- A ring stand and a large ring to support the funnel over the sample jar.
- Two Teflon wash bottles, one which contains a known amount of solvent and is used exclusively for sample recovery and another one used for various solvent rinses outside the sample recovery scheme.
- Clean foil to rest glassware on during recovery procedure.
- Tweezers, spatula, sponge clamp, etc.

The workbench surface is also wiped down with solvent and covered with clean room sheeting.

APPENDIX B*

ANALYTICAL METHODS

INTRODUCTION

This report is a description of the extraction, clean-up, and analysis of samples collected from large combustion sources, such as municipal incinerators, for the possible occurrence of tetrachlorodibenzodioxins (TCDD) and tetrachlorodibenzofurans (TCDF). •The samples received for analysis included particle filters, fly ash, condensates, cyclone solvents, probe rinses, and resins. Until such time as the extractions were carried out, the samples were stored at room temperature in the absence of light. The TCDDs and TCDFs were extracted either in a Soxhlet extractor or by simple solvent extraction procedures, depending on the matrix, before being subjected to a base wash followed by an acid wash. Column chromatography was performed on the samples as a final clean-up step.

The analyses were carried out using packed column GC/HRMS and capillary column GC/HRMS methods. Packed column GC/HRMS was utilized for the determination of total concentration of TCDD and TCDF whereas the isomer specific analyses of those samples designated by SYSTECH in consultation with the EPA were performed by capillary column GC/HRMS.

EXTRACTION PROCEDURES

Impingers

The impinger samples contained two layers: HPLC water and organic, presumably, methylene chloride. The entire sample was spiked with ^{13}C-2,3,7,8-TCDD (internal standard) and stirred for 1 hour with a magnetic stirrer in order to allow the internal standard to partition between water and the organic layers. The water was then separated from the organic layer and extracted three times with hexane (1:1, v/v). Essentially, all the TCDD and TCDF should have been retained in the organic layer.

The organic layer (methylene chloride) was removed by distillation in a distillation apparatus equipped with 30 cm Vigreux column. After the methylene chloride was removed, hexane was added, and the distillation process

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* Appendix B was prepared verbatim from test reports obtained by SYSTECH from Dr. Michael Gross, University of Nebraska.

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was continued further until a final volume of approximately 5 ml of hexane remained. The hexane remaining was combined with the previous hexane extract, and the combined extracts were transferred to a separatory funnel (250 ml). More hexane was added to make a final volume of 75 ml. Then the extract was washed twice with 1F KOH; once with water (15 ml); twice with concentrated sulfuric acid (15 ml each washing); and finally, twice with water (15 ml each washing). The hexane layer was then concentrated and submitted to silica and alumina chromatography (described later).

Particle Filters

The particle filters arrived in a solvent, presumably methylene chloride. A known amount of ^{13}C-2,3,7,8-TCDD was added to the filter and the liquid portion of each sample. The samples (including the filter) were then poured into Soxhlet thimbles, and the solvent was collected in a beaker below the thimble. The filter that was retained in the thimble was extracted with benzene for 3 days. The benzene extract was evaporated under a stream of dry nitrogen and finally replaced with hexane.

In order to replace the original methylene chloride with hexane, a distillation was carried out as described earlier for impingers. The hexane extracts were combined and made up to a volume of 75 ml with more hexane in a separatory funnel. The resulting solution was extracted twice with 1F KOH and then washed with water (25 ml each washing). Repeated extractions were done with concentrated sulfuric acid (15 ml each extraction), and finally the sample was rinsed with water (15 ml). As a final clean-up step, the samples were concentrated and submitted to silica and alumina chromatography.

Resins

The resin samples were received in methylene chloride/methanol (1:1) mixed solutions. The solutions were spiked with a known weight of the internal standard (^{13}C-2,3,7,8-TCDD) and transferred to glass columns (2.5 cm × 30 cm). The methylene chloride/methanol mixture was drained off, and the column was left to dry (1 hour). Subsequently, diethyl ether was added and allowed to equilibrate with the resin for approximately 10 to 20 minutes. Sufficient volume (10 ml/gram of resin) of diethyl ether was passed through the column, and the eluate was collected.

The original methylene chloride/methanol mixture was removed by distillation and replaced by hexane as described earlier for impingers. The resulting hexane extract was combined with the ether eluate, and the solvents were evaporated under a stream of dry nitrogen.

The sample (in hexane) was then transferred to a separatory funnel (250 ml), and more hexane was added to increase the volume to 75 ml. The hexane layer was extracted twice with 1F KOH and washed with water (25 ml). Several extractions were done with concentrated sulfuric acid (15 ml each extraction), and the hexane layer was finally rinsed twice with water (15 ml each washing). The solution was then concentrated and chromatographed on silica followed by alumina columns.

Cyclones, Condensates, and Probe Rinses

Cyclones, condensates, and probe rinse samples were each spiked with the internal standard ^{13}C-2,3,7,8-TCDD. The solvents were replaced with hexane by distillation as previously described.

The resulting hexane extract was made up to a volume of 75 ml with more hexane and extracted twice with 1F KOH, washed with water (15 ml), and repeatedly extracted with concentrated sulfuric acid (15 ml each extraction) followed by rinsing with water (15 ml). The extracts were concentrated and submitted to silica and alumina chromatography.

LIQUID CHROMATOGRAPHY CLEAN-UP

Silica Chromatography

A 5 cm column was prepared using a disposable pipet plugged with glass wool. The silica was capped with 1/4 cm anhydrous sodium sulfate to remove water and then wetted with hexane. The sample, dissolved in 1 ml of hexane, was transferred to the column. TCDD and TCDF were eluted with 3 ml of 20 percent (v/v) benzene in hexane. All the eluate was collected in a 2-oz jar and concentrated to 1 ml. Additional hexane was added, and the sample was again evaporated to 1 ml to reduce the proportion of benzene.

Alumina Chromatography

Alumina was washed by saturating with methylene chloride, removing excess solvent, then activating at 165°C for 24 hours. A column was prepared in the same manner as the silica column above. The column was cooled to room temperature in a desiccator before use.

Hexane was used to wet the column before transferring the sample. The jar was rinsed with 1 ml of hexane which was transferred to the column. The alumina was eluted with two 3-ml portions of pesticide grade CCl_4, then with 4 ml of CH_2Cl_2. These solvents were used to rinse the jar before being transferred to the column. The methylene chloride fraction was collected and concentrated under nitrogen while replacing the volatile CH_2Cl_2 with hexane. All other fractions were discarded.

List of Materials Used in Sample Extraction

Acetone, OmniSolv, MCB
Benzene, OmniSolv, MCB
Carbon tetrachloride, OmniSolv, MCB
Ethyl alcohol, OmniSolv, MCB
Hexane, OmniSolv, MCB, non UV
Methylene chloride, OmniSolv, MCB
Sulfuric acid, concentrated, analytical reagent, Mallinckrodt
Water, distilled in glass
Potassium hydroxide, analytical grade, Mallinckrodt
Sodium sulfate (anhydrous), analytical grade, Fisher

Sodium carbonate (anhydrous), analytical grade, Fisher
Aluminum oxide, neutral, activity grade I, Woelm Pharma
Silica gel, 60 to 200 mesh, reagent grade, Baker Chemical Company
Dry nitrogen (boil-off from liquid N_2)

All OmniSolv line solvents are distilled in glass, suitable for chromatography and residue analysis.

TOTAL TCDD AND TCDF ANALYSES BY PACKED COLUMN GC/HRMS

The sample extracts to be analyzed were kept in centrifuge tubes in a freezer at -4°C. At the time of analysis, the inside of the tubes were washed with hexane or isooctane (approximately 100 µl was used). Subsequently, the solvent was allowed to evaporate to approximately half of its original volume. The remainder was accurately measured with a graduated Hamilton syringe, a major portion (approximately 3/4) returned to the centrifuge tube, and the amount remaining in the syringe was used for GC/HRMS analysis.

Mass Spectrometer

A Kratos MS-50 ultra-high resolution mass spectrometer was used for this analysis (ultimate resolution, 210,000). The mass spectrometer was interfaced via a jet separator to a Perkin Elmer Sigma-II gas liquid chromatograph. For the second batch of samples, a multiple peak monitoring (MPM) accessory was used which enabled us to monitor three ions on three channels. For the first batch of samples, two ions were monitored using the peak matching accessory. The data acquisition was accomplished with a Nicolet Model 1170 signal averaging computer.

Gas Chromatography

A glass column (6 ft × 1/4 in. O.D.) containing HNU Permabond methyl silicone coated with 0.6 percent poly S-179 (HNU Systems, Inc.) was used in the analysis. Typical operating conditions of the gas chromatograph were: helium flow rate of 25 ml/min, injector 275°C, and column temperature program (initial at 250°C and programmed at 10°C/min to 275°C and held at the final temperature until TCDD or TCDF had eluted). The GC/HRMS interface was a simple glass lined stainless steel capillary which was coupled to a glass jet separator. The interface was held at a temperature of 150°C. Signals for the pre-eluters were collected starting at 3.4 and 3.5 minutes for TCDD and TCDF respectively. For the isomers which coelute with 2,3,7,8-TCDD, the respective values were 4.7 and 4.8 minutes. It should be noted that these values correspond with the times at which the signal averaging commenced (the beginning of the peak) and do not represent the actual retention times (peak width at 10 percent height is approximately 40 seconds).

Mass Spectrometric Conditions

The electron impact source was used at 70 eV ionizing energy and an accelerating voltage of 8 KV. The source was set up at 260°C. The instrument was tuned to a resolving power of 10,000 (10 percent valley definition).

For the analysis of TCDD and TCDF in samples from Batch 1, two ions were monitored using the peak matching accessory. For TCDD, the ions of m/z 321.8936 (the most abundant molecular ion having natural isotopic elemental abundances) and m/z 333.9339 (^{13}C-2,3,7,8-TCDD, internal standard) were observed. The internal standard ion along with the most abundant molecular ion having natural isotopic abundances (m/z 305.8986) were monitored in the TCDF analysis. This was carried out for a separate injection.

However, for the analysis of samples from Batch 2, the MPM accessory was used to acquire data on three channels. Thus, the ions of m/z 319.8965, m/z 321.8936, and m/z 333.9339 were monitored for TCDD. For TCDF analysis, a second injection was made, and the ions monitored were m/z 303.9016, m/z 305.8986, and m/z 333.9339. Complete peak profiles were acquired at an amplifier bandwidth of 300 Hz by scanning at a frequency of about 2 Hz, corresponding in each case with a mass range of 200 ppm (0.096 amu). The output of the mass spectrometer was accumulated over about 75 sweeps per channel using a Nicolet Model 1170 signal averager. The resulting signals were submitted to a three-point smoothing routine prior to print out on an X-Y recorder. All the data were acquired as hard copies and also stored on magnetic tape.

Calculation of Results

Quantification was achieved using the internal standard ratio method. Throughout the experiment, standard samples containing 2,3,7,8-TCDD or 2,3,7,8-TCDF and ^{13}C-2,3,7,8-TCDD were analyzed. The slopes of the calibration plots were taken as the averages of the ratios of (I^{334}/ng)/(I^{322}/ng) (I is the normalized intensity for the designated mass) for TCDD and (I^{334}/ng)/(I^{306}/ng) for TCDF obtained using the standard samples.

Residues of TCDD or TCDF in actual samples were calculated by comparing the ratios of intensities of I^{322}/I^{334} (for TCDD) and I^{306}/I^{334} (for TCDF) obtained for a given sample with the slope of the calibration plot. The detection limit was considered to be the respective value obtained for an intensity of 2.5 × noise level measured at the base line.

The internal standard (^{13}C-2,3,7,8-TCDD) was utilized in the calculation of percent recoveries, and in doing so the absolute intensity (I^{334} normalized) was measured and compared with the intensities (I^{334}/ng) obtained by injecting standard solutions of the internal standard. The recovery for TCDF was assumed to be identical to that for TCDD according to this calculation method.

ISOMER SPECIFIC TCDD AND TCDF ANALYSIS BY CAPILLARY COLUMN GC/HRMS

Appropriate dilutions of the samples were made with hexane at the time of analysis, and the aliquots from the resulting solutions were used for capillary column GC/HRMS.

Gas Chromatography/Mass Spectrometer

A Kratos MS-80 medium resolution mass spectrometer (ultimate resolution 20,000) equipped with a 5 channel multiple peak monitoring device was used. The mass spectrometer was coupled to a Carlo-Erba gas chromatograph. The gas chromatograph was equipped with an SE-54 fused silica capillary column (0.25 mm × 30m) which was coupled directly with the ion source.

Gas Chromatographic Conditions

Typical operating conditions were: helium with a linear velocity of ~35 cm/sec, injector 250°C, and detector 275°C. Two temperature programs were utilized in the isomer specific analysis of TCDD and TCDF. For TCDD, the GC parameters were: column temperature 150°C, isothermal for 20 minutes, and then programmed at 5°/min to 280°C. For TCDF analysis, the conditions were: column temperature 150°C, isothermal for 10 minutes, and then programmed at 5°/min to 280°C. A split injection technique was utilized for both types of analysis. The split ratio was approximately 5:1.

Mass Spectrometric Conditions and Multiple Ion Selection

The mass spectrometer was operated in the EI mode (70 eV, 250°C) at 7500 resolving power. Peak profiles were acquired at an amplifier bandwidth of 30,000 Hz. For the TCDD analysis, the ions m/z 319.8965, m/z 321.8936, and m/z 333.9339 (^{13}C-2,3,7,8-TCDD) were monitored on three channels using the MPM. The instrument was tuned using m/z 330.9792 of PFK, and this ion was used as a check mass on Channel 4. For the TCDF analysis, m/z 303.9016, m/z 305.8986, and m/z 333.9339 were monitored on three channels of the MPM. The instrument was tuned using the PFK m/z 304.9824 which was used as a check mass. The output of the mass spectrometer was recorded on a 3-pen strip chart recorder (Linear Model 595).

Calculations of Results

The quantification of the results could have been achieved using the internal standard "ratio method" as for the data from the packed column GC/HRMS analysis. We chose not to do that because the signal for the internal standard, which serves as a reference point in this calculation, was often quite small. Instead, the absolute amounts of each isomer present were calculated by multiplying the fraction of any given isomer present (either TCDD or TCDF) by the value of the total concentration (for TCDD or TCDF) determined in the packed column analyses. The peak height of m/z 322 was used in estimating the percentage (fraction) of any given isomer present in TCDD analysis. Similarly, m/z 306 was used for this purpose in the TCDF analysis. The percentage of any given isomer represents the fraction of the isomer in question (as represented by the peak height of m/z 322 or m/z 306 for TCDD and TCDF respectively) compared with the sum total of all the peak heights detected.

The retention times of the isomers were measured from the point of injection and normalized to the position of the signal of the internal standard, ^{13}C-2,3,7,8-TCDD.

ANALYSIS OF XAD-2 RESIN SAMPLES FOR PENTACHLOROPHENOL (PCP)

Sample Extraction Procedure

Resin samples were made to a slurry with a mixture of dichloromethane and methanol (1:1). The slurry was then transferred to a glass column (1 in. by 8 in.), and the dichloromethane/methanol solvent mixture was subsequently drained off. The resin bed was washed with diethylether (2 ml × 100 ml). The ether effluent was concentrated to a final volume of 5 ml before derivation with diazomethane.

Derivatization of Pentachlorophenol

Pentachlorophenol was derivatized to its methoxy derivative using diazomethane before analysis. Diazomethane was prepared using the reaction of 50 percent potassium hydroxide on N-nitrosomethylurea in ether at 0° to 5°C. An ethereal solution of diazomethane generated was added to the cooled (0° to 5°C) ether effluent, and the resultant mixture was allowed to attain room temperature over a period of half an hour. Finally, excess diazomethane and diethylether were removed with dry nitrogen and replaced with hexane.

Analysis of Pentachlorophenol as Pentachloroanisole by Packed Column GC/HRMS

The sample extracts to be analyzed were kept in centrifuge tubes in a freezer at -4°C. At the time of analysis, the inside of the tubes were washed with hexane or isooctane (approximately 100 µl was used). Subsequently, the solvent was allowed to evaporate to approximately half of its original volume. The remainder was accurately measured with a graduated Hamilton syringe, a major portion (approximately 3/4) returned to the centrifuge tube, and the amount remaining in the syringe was used for GC/HRMS analysis.

Mass Spectrometer--

A Kratos MS-50 ultra-high resolution mass spectrometer was used for this analysis (ultimate resolution, 210,000). The mass spectrometer was interfaced via a jet separator to a Perkin Elmer Sigma-II gas liquid chromatograph. An MPM accessory was used which enabled us to monitor five ions on five channels. The data acquisition was accomplished with a Nicolet Model 1170 signal averaging computer.

Gas Chromatography--

A glass column (6 ft × 1/4 in. O.D.) containing HNU Permabond methyl silicone coated with 0.6 percent poly S-179 (HNU Systems, Inc.) was used in the analysis. Typical operating conditions of the gas chromatograph were: helium flow rate of 25 ml/min, injector 275°C, and column temperature program (initial at 150°C and programmed at 10°C/min to 195°C and held at the final temperature until pentachloroanisole had eluted). The GC/HRMS interface was a simple glass lined stainless steel capillary which was coupled to a glass jet separator. The interface was held at a temperature of 250°C Typical retention time was 3.7 minutes for pentachloroanisole (peak width at 10 percent height approximately 50 seconds).

Mass Spectrometric Conditions--

The electron impact source was used at 70 eV ionizing energy and an accelerating voltage of 8 KV. The source was set up at 260°C. The instrument was tuned to a resolving power of 5000 (10 percent valley definition).

Three ions were monitored using the peak matching accessory, at m/z 279.8597, m/z 281.8568, and m/z 283.8539. The ions at m/z 280, m/z 282, and m/z 284 are the most abundant, the second most abundant, and the third most abundant, respectively, molecular ions of pentachloroanisole. the PFK ions of m/z 280.9824 and 330.9792 were also monitored on two different channels of the MPM as check masses. Complete peak profiles were acquired at an amplifier bandwidth of 3000 Hz by scanning at a frequency of about 2 Hz, corresponding in each case with a mass range of 500 ppm. The output of the mass spectrometer was accumulated over about 75 sweeps per channel using a Nicolet Model 1170 signal averager. The resulting signals were submitted to a three-point smoothing routine prior to print out on an X-Y recorder. All the data were acquired as hard copies and also stored on magnetic tape.

Calculation of Results--

Quantification was achieved by comparing the single ion monitoring response factor for m/z 280 of the standard samples with those of samples. Throughout the experiment standard samples of pentachloroanisole were analyzed. The average value for the response factor of m/z 280 obtained from the standards was compared with the signal response for m/z 280 from the residues of pentachloroanisole in the samples in the quantification. The concentration of pentachlorophenol was evaluated from the results assuming that there was 100 percent conversion of the phenol to anisole. The detection limit was calculated by comparing the intensity of 2.5 × noise level measured at the base line.

The results were validated by comparing the ratios of intensities of m/z 282/280 and m/z 284/280 of the samples with respect to values of the standards. The theoretical values for m/z 282/280 and m/z 284/280 are 0.65 ±0.05 and 0.21 ±0.05 respectively.

ANALYSIS OF WASTE OIL AND FUEL OIL SAMPLES FOR TCDDs AND TCDFs

Sample Extraction Procedure

A sample of 1.0g of oil was added to a solution of acetonitrile (15 ml) in water (70 ml) in a separatory funnel (250 ml). The resulting solution was spiked with the internal standard (^{13}C-2,3,7,8-TCDD) and subsequently extracted with hexane (4 ml × 30 ml). The hexane extract was dried with anhydrous sodium sulfate and concentrated to a final volume of 5 ml.

Alumina Chromatography

Alumina was washed by saturating with methylene chloride, removing excess solvent, then activating at 165°C for 24 hours. After leaving the alumina to cool to room temperature in a desiccator, a column was packed (1 cm × 12 cm) in a similar manner as described for silica chromatography.

The sample was transferred to the column in hexane (5 ml) and washed with hexane (50 ml) and carbon tetrachloride (50 ml). These eluents were discarded. The alumina was subsequently washed with 25 percent methylene chloride in hexane (50 ml). The methylene chloride/hexane eluent was collected and concentrated under dry nitrogen while replacing most of the methylene chloride with hexane.

List of Materials Used in Sample Extraction

Benzene, OmniSolv, MCB
Carbon tetrachloride, OmniSolv, MCB
Hexane, OmniSolv, MCB, non UV
Methylene chloride, OmniSolv, MCB
Water, distilled in glass
Sodium sulfate (anhydrous), analytical grade, Fisher
Aluminum oxide, neutral, activity grade I, Woelm Pharma
Silica gel, 60 to 200 mesh, reagent grade, Baker Chemical Company
Dry nitrogen (boil-off from liquid N_2)

All OmniSolv line solvents are distilled in glass, suitable for chromatography and residue analysis.

TCDD and TCDF Analysis by Capillary Column GC/HRMS

Appropriate dilutions of the samples were made with hexane at the time of analysis, and the aliquots from the resulting solutions were used for capillary column GC/HRMS.

Gas Chromatography/Mass Spectrometer

A Kratos MS-80 medium resolution mass spectrometer (ultimate resolution 20,000) equipped with a five channel MPM device was used. The mass spectrometer was coupled to a Carlo-Erba gas chromatograph. the gas chromatograph was equipped with as SE-54 fused silica capillary column (0.25 mm × 30m) which was coupled directly with the ion source.

Gas Chromatographic Conditions

Typical operating conditions were: helium with a linear velocity of ~35 cm/sec, injector 250°C, and detector 275°C. For TCDD and TCDF the GC parameters were: column temperature 200°C (initial) and then programmed at 5°/min to 280°C.

Mass Spectrometric Conditions and Multiple Ion Selection

The mass spectrometer was operated in the EI mode (70 eV, 250°C) at 3000 resolving power. Peak profiles were acquired at an amplifier bandwidth of 30,000 Hz. For the TCDD analysis, the ions m/z 319.8965, m/z 321.8936, and m/z 333.9339 (^{13}C-2,3,7,8-TCDD) were monitored on three channels using the MPM. The instrument was tuned using m/z 330.9792 of PFK, and this ion was used as a check mass on Channel 4. For the TCDF analysis, m/z 303.9016, m/z 305.8986, and m/z 333.9339 were monitored on three channels of the MPM. The instrument was tuned using the PFK m/z 304.8924 as a check mass. The output of the mass spectrometer was recorded on a three-pen strip chart recorder (Linear Model 595).

Calculation of Results

Quantification was achieved using the internal standard ratio method. Throughout the experiment, standard samples containing 2,3,7,8-TCDD or 2,3,7,8-TCDD and ^{13}C-2,3,7,8-TCDD were analyzed. The slopes of the calibration plots were taken as the averages of the ratios of $(I^{334}/ng)/(I^{322}/ng)$ (I is the normalized intensity for the designated mass) for TCDD and $(I^{334}/ng)/(I^{306}/ng)$ for TCDF obtained using the standard samples.

Residues of TCDD or TCDF in actual samples were calculated by comparing the ratios of intensities of I^{322}/I^{334} (for TCDD) and I^{306}/I^{344} (for TCDF) obtained for a given sample with the slope of the calibration plot. The detection limit was considered to be the respective value obtained for an intensity of 2.5 × noise level measured at the base line.

The internal standard (^{13}C-2,3,7,8-TCDD) was utilized in the calculation of percent recoveries, and in doing so, the absolute intensity (I^{334} normalized) was measured and compared with the intensities (I^{334}/ng) obtained by injecting standard solutions of the internal standard. the recovery for TCDF was assumed to be identical to that for TCDD according to this calculation method.

APPENDIX C

TEST DATA

APPENDIX C

TEST DATA

Appendix C includes a sample calculation sheet illustrating the method used in computing emission rates of TCDDs and TCDFs in this program. Also included are Tables C-1 through C-6 which summarize the data obtained on all stack gas samples, combustion air samples, and associated method blanks. In these tables the sign < is employed to indicate the instrumental detection limit when no TCDD or TCDF was actually detected in the sampling train components. Totals for samples which contained components with no detectable levels of TCDD or TCDF have been expressed as ranges. The lower ends of the ranges represent the amounts actually detected in the samples while the upper ends include the amount actually detected plus the detection limits of those components in which none was detected. Finally, Appendix C also includes the complete set of data submitted to SYSTECH by Dr. Michael Gross. These sheets are keyed to Tables C-1 through C-6 by analytical sample numbers.

SAMPLE CALCULATION SHEET - MODIFIED METHOD 5 DATA

September 18, 1980 - Facility A

1. ANALYTICAL DATA

Sample component	Mass of Micropollutants Found			
	Total TCDD (pg)	Maximum 2,3,7,8-TCDD (pg)	Total TCDF (pg)	Maximum 2,3,7,8-TCDF (pg)
Probe and filter	≤ 180	≤ 90	720	350
XAD resin	6,700	1,800	88,000	50,000
Impingers	*	*	*	*
TOTAL	6,790 ±90	1,845 ±45	88,720	50,350

2. SAMPLE VOLUME

A. Sample dry gas volume at standard conditions

$$V_{m(std)} = \frac{(70 + 460)\ ^\circ R}{29.92 \text{ in Hg}} \left(\frac{V_m}{T_m\ ^\circ R} \right) \left(P_b + \frac{\Delta H}{13.6 \text{ in } H_2O/\text{in Hg}} \right) \delta$$

Where: $V_{m(std)}$ = dry gas volume at 70°F and 29.92 in Hg

V_m = actual dry gas volume (ft^3)

T_m = actual temperature (°R)

P_b = barometric pressure (in Hg)

ΔH = pressure drop (in H_2O)

δ = volumetric correction factor

$$V_{m(std)} = 17.71 \left(\frac{218.432}{551} \right) \left(29.96 + \frac{1.56}{13.6} \right) .99 = 209.035 \text{ SCF}$$

* Indicates no data available.

B. Sample water volume at standard conditions

$$V_{w(std)} = \frac{0.0474\ ft^3}{m\ell} \quad V_{1c}$$

Where: $V_{w(std)}$ = water volume at 70°F and 29.92 in. Hg (SCF)

V_{1c} = weight of water collected in impingers (g)

$V_{w(std)}$ = (.0474) (335) = 15.88 SCF

C. Total sample volume at standard conditions

$V_{t(std)} = V_{m(std)} + V_{w(std)}$

Where: $V_{t(std)}$ = gas volume at 70°F and 29.92 in Hg (SCF)

$V_{t(std)}$ = 209.035 + 15.88 = 224.914 SCF

3. MICROPOLLUTANT CONCENTRATION IN SAMPLE

$$\frac{pg}{m^3} = \frac{pg\ measured}{224.914\ SCF} \times \frac{SCF}{m^3 \times .02832}$$

$$ppt\ (TCDD) = \frac{pg}{m^3} \times \frac{g}{10^{12} pg} \times \frac{mole\ TCDD}{322 g} \times$$

$$\frac{24.06\ell\ air}{mole\ @\ 70°F\ \&\ 29.92\ in.\ Hg} \times \frac{m^3}{10^3 \ell} \times 10^{12}$$

$$ppt\ (TCDF) = \frac{pg}{m^3} \times \frac{g}{10^{12} pg} \times \frac{mole\ TCDF}{306 g} \times$$

$$\frac{24.09\ell\ air}{mole\ @\ 70°F\ \&\ 29.92\ in.\ Hg} \times \frac{m^3}{10^3 \ell} \times 10^{12}$$

Sample Component Concentration of Micropollutants in Sample

(Total rounded to significant figures only)

Sample Component	Total TCDD		Maximum 2,3,7,8-TCDD		Total TCDF		Maximum 2,3,7,8-TCDF	
	pg/m^3	ppt	pg/m^3	ppt	pg/m^3	ppt	pg/m^3	ppt
Probe and filter	<28		<14		113		55	
XAD resin	1,052		283		13,816		7,850	
Impingers	---		---		---		---	
TOTAL	<1,100	<.082	<290	<.022	14,000	<1.1	7,900	.62

4. STACK FLOW RATE

A. Mass of fuel burned in 63.75-hr test
198,960 lb wet (151,667 lb dry)

B. Mass of residue produced
47,175 lb wet (29,013 lb dry)
(1,973 combustibles)

C. Excess air level (EA) at stack

$$EA = \frac{O_2}{.2682\ N_2 - O_2} = \frac{16.2}{.2682(80.4) - 16.2} = 3.02$$

D. Stoichiometric air requirement (SA) dry basis

$$SA = 11.53(C) + 34.34(H) + 4.29(S) - 4.29(O)$$

Where: C = carbon fraction in fuel (corrected for combustibles lost in ash)

H = hydrogen fraction in fuel

S = oxygen fraction in fuel

$$SA = 11.53(.4104) + 34.34(.0637) + 4.29(.0011) - 4.29(.3114) =$$

5.58 lb air/lb fuel dry

E. Total dry flue gas mass

$TDFG = Fd\ (SA)\ (1 + EA) + (Fd - Rd) - 9\ (Fd_{H_2})$

Where: TDFG = total dry flue gas (lb)

Fd = dry fuel (lb)

Rd = dry residue (lb)

Fd_{H_2} = hydrogen in dry fuel (lb)

$TDFG = 151{,}667\ (5.58)\ (4.02) + (141{,}667 - 29{,}013) - 9\ (9662)$ lb dry

$= 3.443 \times 10^6$ lb dry

F. Total wet flue gas mass

$TWFG = Fd_{H_2O} + 9(Fd_{H_2}) + (HR)\ (Fd)\ (SA)\ (1 + EA)$

Where: TWFG = total water in flue gas (lb)

Fd_{H_2O} = moisture in fuel (lb)

HR = humidity ratio (lb H_2O/lb dry air)

$TWFG = 47{,}293 + 9(9{,}662) + (.006)\ (151{,}667)\ (5.58)\ (4.02)$

$= 154.693 \times 10^3$ lb

G. Total flue gas (TFG) mass

$TFG = TDFG + TWFG$

$TFG = 3.443 \times 10^6 + 154.693 \times 10^3 = 3.5977 \times 10^6$ lb flue gas

H. Total flue gas volume

1) Molecular weight of flue gas

M_{Fw} = mass fraction of water in flue gas $= \dfrac{154{,}693}{3.5977 \times 10^6} = .043$

M_{FD} = mass fraction of dry gas in flue gas $= 1 - M_{Fw} = .957$

Flue gas component	Volume percent	Mass/mole (lb/mole)	Mass fraction dry (lb/lb)	Mass fraction wet (lb/lb)
CO_2	3.4	1.496	.0512	.049
O_2	16.2	5.184	.1776	.170
N_2	80.4	22.512	.7712	.738
H_2O	---	---	---	.043
TOTAL	100.0	29.192	1.0000	1.000

Flue gas component	Mass fraction wet (lb/lb)	Mole fraction wet (mole/lb)
CO_2	.049	1.114×10^{-3}
O_2	.170	5.313×10^{-3}
N_2	.738	26.357×10^{-3}
H_2O	.043	2.389×10^{-3}
TOTAL	1.000	35.173×10^{-3} mole/lb

$$\text{Molecular weight of wet flue gas} = \frac{1}{37.173 \times 10^{-3}\ \text{mole/lb}} = 28.43\ \text{lb/mole}$$

2) Molar volume of wet flue gas at 70°F and 29.92 in Hg

$$V = \frac{n\ RT}{P}$$

Where: V = molar volume $\frac{ft^3}{mole_{lb}}$

n = 1 mole

$$R = \frac{21.8\ \text{ft}^3\ \text{in Hg}}{\text{mole}_{1b}\ {}^\circ\text{R}}$$

$$T = (70 + 460)\ {}^\circ\text{R}$$

$$P = 29.92\ \text{in Hg}$$

$$V = \frac{(21.8)\ (530)}{29.92} = 386\ \text{ft}^3/\text{mole}_{1b}\ \text{flue gas}$$

3) Total flue gas volume

$$V = \frac{\text{TFG}}{\text{lb/mole}_{1b}} \times \frac{386\ \text{ft}^3}{\text{mole}_{1b}\ \text{flue gas}}\ \text{SCF}$$

$$= \frac{3.5977 \times 10^6}{28.43} \times 386 = 48.847 \times 10^6\ \text{SCF}$$

I. Flue gas flow rate

$$\text{Flow rate} = \frac{\text{Volume}}{\text{Time}}$$

$$= \frac{48.847 \times 10^6\ \text{SCF}}{63.75\ \text{hr}} \times \frac{\text{hr}}{60\ \text{min}}$$

$$= 12{,}770\ \text{SCFM}$$

$$= 361.62\ \text{SCMM}$$

J. Micropollutant emission rates

$$\frac{\text{g}}{\text{sec}} = \frac{\text{pg}}{\text{m}^3} \times \frac{\text{g}}{10^{12}\text{pg}} \times 361.62\ \text{SCMM} \times \frac{\text{min}}{60\ \text{sec}}$$

$$\frac{\text{g}}{\text{ton fuel fired}} = \frac{\text{g}}{\text{sec}} \times \frac{60\ \text{sec}}{\text{min}} \times \frac{60\ \text{min}}{\text{hr}} \times \frac{63.75\ \text{hr}}{\left(\frac{198{,}960}{2{,}000}\right)\ \text{tons fuel fired}}$$

Emission Rate of Micropollutants

(Rounded to significant figures only)

Total TCDD		Maximum 2,3,7,8-TCDD	
g/sec	g/ton fired	g/sec	g/ton fired
6.0×10^{-9}	1.4×10^{-5}	1.6×10^{-9}	3.7×10^{-6}

Total TCDF		Maximum 2,3,7,8-TCDF	
g/sec	g/ton fired	g/sec	g/ton fired
7.8×10^{-8}	1.8×10^{-4}	4.4×10^{-8}	1.0×10^{-4}

TABLE C-1. FACILITY A - TCDD DATA

			TCDD									
			Total TCDD					Maximum 2,3,7,8-TCDD				
Sample	Sample component	Analytical sample No.	Mass found (pg)	Concentration in sample (pg/m^3)	Concentration in sample (ppt)	Emission rate (g/sec)	Emission rate (g/ton fired)	Mass found (pg)	Concentration in sample (pg/m^3)	Concentration in sample (ppt)	Emission rate (g/sec)	Emission rate (g/ton fired)
Modified Method 5 (9/18/80)	Probe and filter	4	≤ 180					≤ 90				
	XAD resin	5	6,700					1,800				
	Impingers	*	*					*				
	Total		6,790±90	1,100	.082	6.0×10^{-9}	1.4×10^{-5}	1,845±45	290	.022	1.6×10^{-9}	3.7×10^{-6}
Modified Method 5 (10/15/80) (Blank)†	Probe and filter	6	≤ 90					≤ 40				
	XAD resin	7	≤ 195					≤ 85				
	Impingers	*	*					*				
	Total		≤ 285	≤ 57	≤ .004	NA	NA	≤ 125	≤ 25	≤ .002	NA	NA
Modified Method 5 (10/22/80)	Probe and filter	1	700					190				
	XAD resin	2	10,800					2,400				
	Impingers	3	≤ 75					≤ 30				
	Total		11,538±38	1,300	.097	9.0×10^{-9}	1.5×10^{-5}	2,605±15	300	.02	2.0×10^{-9}	3.4×10^{-6}
SASS train (9/12/80) (Blank)	Probe	I-5	≤ 200					≤ 200				
	Cyclones	I-1,2,3	≤ 500					≤ 500				
	Filter	I-4	≤ 60					≤ 60				
	Resin and condensate	I-6,7	≤ 200§					≤ 200§				
	Impingers	*	*					*				
	Total		≤ 960	≤ 30	≤ .002	NA	NA	≤ 960	≤ 30	≤ .002	NA	NA

TABLE C-1. (continued)

			TCDD									
			Total TCDD					Maximum 2,3,7,8-TCDD				
Sample	Sample component	Analytical sample No.	Mass found (pg)	Concentration in sample (pg/m^3)	Concentration in sample (ppt)	Emission rate (g/sec)	Emission rate (g/ton fired)	Mass found (pg)	Concentration in sample (pg/m^3)	Concentration in sample (ppt)	Emission rate (g/sec)	Emission rate (g/ton fired)
SASS train (9/16/80)	Probe	I-13	≤ 290					200				
	Cyclones	I-9,10,11	2,600					1,300				
	Filter	I-12	≤ 60					≤ 60				
	Resin and condensate	I-14,15	148,140					60,320				
	Impingers	*	*					*				
	Total		150,915±175	8,400±10	.63	4.7×10^{-8}	1.1×10^{-4}	61,850±30	3,500	.26	2.0×10^{-8}	4.6×10^{-5}
SASS train (10/23/80)	Probe	A-4	≤ 260					≤ 160				
	Cyclones	A-6,7,8	1,300±20					730				
	Filter	A-5	580					400				
	Resin and condensate	A-2,3	29,700					5,400				
	Impingers	A-1	1,050					360				
	Total		32,760±150	1,400±10	.110	9.6×10^{-9}	1.6×10^{-5}	6,970±80	310	.023	2.0×10^{-9}	3.5×10^{-6}

Notes:

* Samples not analyzed.

† No air drawn through train; concentrations computed from average volume drawn through stack trains on 9/18/80 and 10/22/80 (4.98 dscm).

§ No data available for resin only.

≤ Indicates none detected at level shown.

NA Not applicable.

Concentration and emission rates have been rounded to include significant figures only.

TABLE C-2. FACILITY A - TCDF DATA

			TCDF									
			Total TCDF					Maximum 2,3,7,8-TCDF				
Sample	Sample component	Analytical sample No.	Mass found (pg)	Concentration in sample (pg/m^3)	Concentration in sample (ppt)	Emission rate (g/sec)	Emission rate (g/ton fired)	Mass found (pg)	Concentration in sample (pg/m^3)	Concentration in sample (ppt)	Emission rate (g/sec)	Emission rate (g/ton fired)
Modified Method 5 (9/18/80)	Probe and filter	4	720					350				
	XAD resin	5	88,000					50,000				
	Impingers	*	*					*				
	Total		88,720	14,000	1.1	7.8×10^{-8}	1.8×10^{-4}	50,350	7,900	.62	4.4×10^{-8}	1.0×10^{-4}
Modified Method 5 (10/15/80) (Blank)†	Probe and filter	6	≤ 400					≤ 210				
	XAD resin	7	321,500§					320,000§				
	Impingers	*	*					*				
	Total		≤ 400	≤ 120	≤ .009	NA	NA	≤ 210	≤ 40	≤ .003	NA	NA
Modified Method 5 (10/22/80)	Probe and filter	1	10,000					3,900				
	XAD resin	2	60,000					20,000				
	Impingers	3	1,070					420				
	Total		71,070	8,300	.65	5.5×10^{-8}	9.4×10^{-5}	24,320	2,800	.22	1.9×10^{-8}	3.2×10^{-5}
SASS train (9/12/80) (Blank)	All	*	*					*				
SASS train (9/16/80)	All	*	*					*				

TABLE C-2. (continued)

			TCDD									
			Total TCDD					Maximum 2,3,7,8-TCDD				
Sample	Sample component	Analytical sample No.	Mass found (pg)	Concentration in sample (pg/m^3)	Concentration in sample (ppt)	Emission rate (g/sec)	Emission rate (g/ton fired)	Mass found (pg)	Concentration in sample (pg/m^3)	Concentration in sample (ppt)	Emission rate (g/sec)	Emission rate (g/ton fired)
SASS train (10/23/80)	Probe	A-4	670±100					≦ 570				
	Cyclones	A-6,7,8	6,600					3,610				
	Filter	A-5	2,500					1,000				
	Resin and condensate	A-2,3	355,500					125,200				
	Impingers	A-1	10,500					5,900				
	Total		375,880±50	17,000	1.3	1.1×10^{-7}	1.9×10^{-4}	136,280	6,000	.50	4.0×10^{-8}	6.8×10^{-5}

Notes:

* Samples not analyzed.

† No air drawn through train; concentrations computed from average volume drawn through stack trains on 9/18/80 and 10/22/80 (4.98 dscm).

§ These data were found to be an analytical artifact and are not include in the sample total.

≦ Indicates none detected at level shown.

NA Not applicable.

Concentration and emission rates have been rounded to include significant figures only.

TABLE C-3. FACILITY B - TCDD DATA

			TCDD									
			Total TCDD					Maximum 2,3,7,8-TCDD				
Sample	Sample component	Analytical sample No.	Mass found (pg)	Concentration in sample (pg/m^3)	Concentration in sample (ppt)	Emisson rat (g/sec)	Emisson rat (gton fired)	Mass found (pg)	Concentration in sample (pg/m^3)	Concentration in sample (ppt)	Emission rate (g/sec)	Emission rate (g/ton fired)
Modified Method 5 (12/5/80) (Blank)	Probe and filter	8	7,980					980				
	XAD resin	9	≤ 175					≤ 90				
	Impingers	*	*					*				
	Total		8,068±88	1,060	.079	NA	NA	1,025±45	130	.009	NA	NA
Modified Method 5 (12/8/80)	Probe and filter	11	10,900					9,100				
	XAD resin	12	25,000					13,000				
	Impingers	13	155±45					110				
	Total		36,055±45	4,400	.33	1.8×10^{-8}	5.1×10^{-5}	22,210	2,700	.20	1.1×10^{-8}	3.1×10^{-5}
Modified Method 5 (12/9/80)	Probe and filter	17	5,300					1,300				
	XAD resin	18	41,000					13,000				
	Impingers	*	*					*				
	Total		46,300	3,800	.28	1.4×10^{-8}	4.4×10^{-5}	14,300	1,200	.090	4.2×10^{-9}	1.3×10^{-5}
Modified Method 5 (12/10/80)	Probe and filter	22	5,030					2,330				
	XAD resin	23	26,000					11,000				
	Impingers	*	*					*				
	Total		31,030	2,500	.19	8.9×10^{-9}	2.8×10^{-5}	13,330	1,100	.082	3.8×10^{-9}	1.2×10^{-5}
Combustion air - resin train (12/5/80) (Blank)	XAD resin	10	≤ 200					≤ 100				
	Impingers	*	*					*				
	Total		≤ 200	≤ 10	≤ .0007	NA	NA	≤ 100	≤ 5	≤ .0004	NA	NA
Combustion air - resin train (12/8/80)	XAD resin	14	≤ 135					≤ 55				
	Impingers	*	*					*				
	Total		≤ 135	≤ 4	≤ .0003	NA	NA	≤ 55	≤ 2	≤ .0001	NA	NA

(continued)

TABLE C-3. (continued)

			TCDD									
			Total TCDD					Maximum 2,3,7,8-TCDD				
				Concentration in sample		Emission rate			Concentration in sample		Emission rate	
Sample	Sample component	Analytical sample No.	Mass found (pg)	(pg/m^3)	(ppt)	(g/sec)	(g/ton fired)	Mass found (pg)	(pg/m^3)	(ppt)	(g/sec)	(g/ton fired)
Combustion air - resin train (12/9/80)	XAD resin Impingers Total	19 20	≤ 160 ≤ 90 ≤ 250	≤ 9	≤.0007	NA	NA	≤ 80 ≤ 40 ≤ 120	≤ 4	≤.0003	NA	NA
Combustion air - resin train (12/10/81)	XAD resin Impingers Total	24 *	≤ 200 * ≤ 200	≤ 5	≤.0004	NA	NA	≤ 90 * ≤ 90	≤ 2	≤.0002	NA	NA
Combustion air† - Hi Vol (12/7/80) (Blank)	Filter	15	135	NA	NA	NA	NA	55	NA	NA	NA	NA
Combustion air - Hi Vol (12/8/80)	Filter	16	770	.31	2.3×10^{-5}	NA	NA	290	.12	9.0×10^{-6}	NA	NA
Combustion air - Hi Vol (12/9/80)	Filter	21	980	.39	2.9×10^{-5}	NA	NA	390	.16	1.2×10^{-5}	NA	NA
Combustion air - Hi Vol (12/10/80)	Filter	25	590	.24	1.8×10^{-5}	NA	NA	190	.076	5.7×10^{-6}	NA	NA

Notes:

* Samples not analyzed.
† No air drawn through train.
≤ Indicates none detected at level shown.
NA Not applicable.
Concentration and emission rates have been rounded to include significant figures only.

TABLE C-4. FACILITY B - TCDF DATA

			TCDF									
			Total TCDF					Maximum 2,3,7,8-TCDF				
				Concentration in sample		Emission rate			Concentration in sample		Emission rate	
Sample	Sample component	Analytical sample No.	Mass found (pg)	(pg/m^3)	(ppt)	(g/sec)	(g/ton fired)	Mass found (pg)	(pg/m^3)	(ppt)	(g/sec)	(g/ton fired)
Modified Method 5 (12/5/80) (Blank)	Probe and filter	8	≤ 820					≤ 390				
	XAD resin	9	790 ±330					460				
	Impingers	*	*					*				
	Total		1,200 ± 740	160 ± 97	.012 ±.0076	NA	NA	655 ±195	93 ±32	.0073 ±.0025	NA	NA
Modified Method 5 (12/8/80)	Probe and filter	11	125,000					60,000				
	XAD resin	12	260,000					134,000				
	Impingers	13	1,240 *					500				
	Total		386,240	47,700	3.75	1.9×10^{-7}	5.6×10^{-4}	194,500	24,000	1.9	9.7×10^{-8}	2.7×10^{-4}
Modified Method 5 (12/9/80)	Probe and filter	17	31,000					15,000				
	XAD resin	18	23,600					8,600				
	Impingers	*	*					*				
	Total		54,600	4,500	.37	1.6×10^{-8}	5.0×10^{-5}	23,600	1,900	.15	7.0×10^{-9}	2.2×10^{-5}
Modified Method 5 (12/10/80)	Probe and filter	22	23,600					9,600				
	XAD resin	23	112,000					51,000				
	Impingers	*	*					*				
	Total		135,600	10,900	.86	3.9×10^{-8}	1.2×10^{-4}	60,600	4,900	.19	1.7×10^{-8}	5.1×10^{-5}
Combustion air-resin train (12/5/80) (Blank)	XAD resin	10	≤ 510					≤ 260				
	Impingers	*	*					*				
	Total		≤ 510	≤ 28	≤ .0022	NA	NA	≤ 260	≤ 14	≤ .0011	NA	NA
Combustion air-resin train (12/8/80)	XAD resin	14	≤ 390					≤ 140				
	Impingers	*	*					*				
	Total		≤ 390	≤ 11	≤ .0086	NA	NA	≤ 140	≤ 3.9	≤ .00031	NA	NA

(Continued)

TABLE C-4. (continued)

Sample	Sample component	Analytical sample No.	TCDF: Total TCDF: Mass found (pg)	TCDF: Total TCDF: Concentration in sample (pg/m^3)	TCDF: Total TCDF: Concentration in sample (ppt)	TCDF: Total TCDF: Emission rate (g/sec)	TCDF: Total TCDF: Emission rate (g/ton fired)	TCDF: Maximum 2,3,7,8-TCDF: Mass found (pg)	TCDF: Maximum 2,3,7,8-TCDF: Concentration in sample (pg/m^3)	TCDF: Maximum 2,3,7,8-TCDF: Concentration in sample (ppt)	TCDF: Maximum 2,3,7,8-TCDF: Emission rate (g/sec)	TCDF: Maximum 2,3,7,8-TCDF: Emission rate (g/ton fired)
Combustion air-resin train (12/9/80)	XAD resin Impingers Total	19 20	≤ 250 ≤ 100 ≤ 350	≤ 13	≤ .0010	NA	NA	≤ 110 ≤ 45 ≤ 155	≤ 5.5	≤ .00043	NA	NA
Combustion air-resin train (12/10/80)	XAD resin Impingers Total	24 *	≤ 175 * ≤ 175	≤ 4.2	≤ .00033			≤ 55 * ≤ 55	≤ 1.3	≤ .00010	NA	NA
Combustion air-HI Vol (12/7/80) (Blank)	Filter	15	220 ±20	NA	NA	NA	NA	200	NA	NA	NA	NA
Combustion air-HI Vol (12/8/80)	Filter	16	2,140	.86	6.8×10^{-5}	NA	NA	1,200	.48	3.8×10^{-5}	NA	NA
Combustion air-HI Vol (12/9/80)	Filter	21	2,100	.84	6.6×10^{-5}	NA	NA	1,000	.40	3.0×10^{-5}	NA	NA
Combustion air-HI Vol (12/10/80)	Filter	25	≤ 1,200	≤ .48	≤ 3.8×10^{-5}	NA	NA	≤ 450	≤ .18	≤ 1.4×10^{-5}	NA	NA

* Samples not analyzed.

‡ No air drawn through train

≤ Indicates none detected at level shown

NA Not applicable

Concentration and emission rates have been rounded to include significant figures only.

TABLE C-5. FACILITY C - TCDD DATA

			TCDD									
			Total TCDD					Maximum 2,3,7,8-TCDD				
				Concentration in sample		Emission rate			Concentration in sample		Emission rate	
Sample	Sample component	Analytical sample No.	Mass found (pg)	(pg/m^3)	(ppt)	(g/sec)	(g/ton fired)	Mass found (pg)	(pg/m^3)	(ppt)	(g/sec)	(g/ton fired)
Modified Method 5 (2/27/81) (Blank)	Probe and filter	28	5,300					2,100				
	XAD resin	29	≤ 135					≤ 70				
	Impingers	30	≤ 45					≤ 45				
	Total		5,390 ±90	920	.068	NA	NA	2,158 ±58	370 ±10	.028	NA	NA
Modified Method 5 (4/1/81)	Probe and filter	31	1,160					460				
	XAD resin	32	367,000					118,000				
	Impingers	33	5,700					1,300				
	Total		373,860	30,000	2.2	2.1×10^{-7}	3.3×10^{-4}	119,760	9,600	.72	6.7×10^{-8}	1.0×10^{-4}
Modified Method 5 (4/7/81)	Probe and filter	38	1,020					370				
	XAD resin	39	338,000					98,000				
	Impingers	*	*					*				
	Total		339,020	29,500	2.2	2.38×10^{-7}	6.3×10^{-4}	98,370	8,600	.64	6.9×10^{-8}	1.8×10^{-4}
Combustion air - resin train (2/27/81) (Blank)	XAD resin	26	≤ 330					≤ 190				
	Impingers	27	≤ 20					≤ 20				
	Total		≤ 350	≤ 14	≤ .0010	NA	NA	≤ 210	≤ 8.6	≤ .0006	NA	NA

(continued)

TABLE C-5. (continued)

			TCDD									
			Total TCDD					Maximum 2,3,7,8-TCDD				
Sample	Sample component	Analytical sample No.	Mass found (pg)	Concentration in sample (pg/m^3)	Concentration in sample (ppt)	Emission rate (g/sec)	Emission rate (g/ton fired)	Mass found (pg)	Concentration in sample (pg/m^3)	Concentration in sample (ppt)	Emission rate (g/sec)	Emission rate (g/ton fired)
Combustion air - resin train (4/1/81)	XAD resin Impingers Total	34 35	490 1,280 1,770	480	.036	NA	NA	170 290 460	120	.009	NA	NA
Combustion air - resin (4/7/81)	XAD resin Impingers Total	40 *	310 ±70 * 310 ±70	29 ±7	.0022±.0005	NA	NA	≤ 140 * ≤ 140	≤ 13	≤.001	NA	NA
Combustion air - Hi Vol† (4/1/81) (Blank)	Filter	37	≤ 150	NA	NA	NA	NA	≤ 150	NA	NA	NA	NA
Combustion air - Hi Vol (4/1/81)	Filter	36	≤ 490	≤.58	≤4.3 × 10-5	NA	NA	≤ 200	≤.2	≤.00001	NA	NA
Combustion air - Hi Vol (4/7/81)	Filter	41	≤ 230	≤.25	≤1.9 × 10^{-5}	NA	NA	≤ 110	≤.12	≤.00001	NA	NA

Notes:

* Samples not analyzed.
† No air drawn through train.
≤ Indicates none detected at level shown.
NA Not applicable.
Concentration and emission rates have been rounded to include significant figures only.

TABLE C-6. FACILITY C - TCDF DATA

			TCDF									
			Total TCDF					Maximum 2,3,7,8-TCDF				
				Concentration in sample		Emission rate			Concentration in sample		Emission rate	
Sample	Sample component	Analytical Sample No.	Mass found (pg)	(pg/m^3)	(ppt)	(g/sec)	(g/ton fired)	Mass found (pg)	(pg/m^3)	(ppt)	(g/sec)	(g/ton fired)
Modified Method 5 (2/27/81) (Blank)	Probe and filter	28	≤ 380					≤ 140				
	XAD resin	29	≤ 100					≤ 60				
	Impingers	30	≤ 240					≤ 110				
	Total		≤ 720	≤120	≤.0094	NA	NA	≤ 310	≤53	≤.0042	NA	NA
Modified Method 5 (4/1/81)	Probe and filter	31	10,100					4,400				
	XAD resin	32	3,670,000					1,420,000				
	Impingers	33	234,000					10,000				
	Total		3,914,100	312,000	24.5	2.17×10^{-6}	3.4×10^{-3}	1,434,400	114,000	8.96	7.97×10^{-7}	1.2×10^{-3}
Modified Method 5 (4/7/81)	Probe and filter	38	4,000					1,700				
	XAD resin	39	2,840,000					980,000				
	Impingers	*	*					*				
	Total		2,844,000	247,000	19.4	2.00×10^{-6}	5.3×10^{-3}	981,700	85,000	6.68	6.91×10^{-7}	1.8×10^{-3}
Combustion air - resin train (2/27/81) (Blank)	XAD resin	26	≤ 185					≤ 95				
	Impingers	27	≤ 50					≤ 25				
	Total		≤ 235	≤9.6	≤.00075	NA	NA	≤120	≤ 4.9	≤.00039	NA	NA

TABLE C-6. (continued)

			TCDF									
			Total TCDF					Maximum 2,3,7,8-TCDF				
				Concentration in sample		Emission rate			Concentration in sample		Emission rate	
Sample	Sample component	Analytical sample No.	Mass found (pg)	(pg/m^3)	(ppt)	(g/sec)	(g/ton fired)	Mass found (pg)	(pg/m^3)	(ppt)	(g/sec)	(g/ton fired)
Combustion air - resin train (4/1/81)	XAD resin Impingers Total	34 35	≤ 345 4,600 4,773±173	1,300±50	.10±.004	NA	NA	≤ 160 2,300 2,380±80	640±20	.050±.002	NA	NA
Combustion air - resin (4/7/81)	XAD resin Impingers Total	40 *	≤ 560 * ≤ 560	≤ 53	≤ .0042	NA	NA	≤ 250 * ≤ 250	≤ 24	≤ .0019	NA	NA
Combustion air - Hi Vol† (4/1/81) (Blank)	Filter	37	≤ 150	NA	NA	NA	NA	≤ 65	NA	NA	NA	NA
Combustion air - Hi Vol (4/1/81)	Filter	36	405±55	.48±.06	3.8×10^{-5} $\pm 5 \times 10^{-6}$	NA	NA	≤ 110	≤ .13	≤ 1.0×10^{-5}	NA	NA
Combustion air - Hi Vol (4/7/81)	Filter	41	≤ 110	≤ .12	≤ 9.4×10^{-6}	NA	NA	≤ 40	≤ .04	≤ 3.0×10^{-6}	NA	NA

Notes:

* Samples not analyzed.

† No air drawn through train.

≤ Indicates none detected at level shown.

NA Not applicable.

Concentration and emission rates have been rounded to include significant figures only.

The following is the complete set of data submitted to SYSTECH by Dr. Michael Gross of the University of Nebraska.

ANALYSIS OF COMBUSTION RELATED SAMPLES FOR 2,3,7,8-TCDD AND CO-ELUTING AND PRE-ELUTING ISOMERS BY GAS LIQUID CHROMATOGRAPHY/HIGH RESOLUTION MASS SPECTROMETRY

				2,3,7,8-TCDD and Co-eluters			Pre-eluters			
Analytical sample no.	Nature of sample	Sample wt. or percent analyzed	Ng spike added	Conc. (ppb)[1] or amount (ng)	Detection limit	Isotope[2] ratio	Conc. (ppb)[1] or amount (ng)	Detection limit	Isotope[2] ratio	Percent recovery
No. 1[3]	Blank	100	3.0 ng	nd	<.02 ng					65
I-1	Cyclone	26	2.5	nd	0.2 ng					40
I-2	Cyclone	17	2.5	nd	0.2 ng					75
I-3	Cyclone	25	2.5	nd	0.1 ng					80
I-4	Particle filter	100	3.0	nd	0.06 ng					50
I-5	Probe rinse	25	2.5	nd	0.2 ng					70
No. 2[3]	Blank	100	3.0	nd	<.001					100
I-6	XAD-resin	15.09 g	3.0							0
I-7	Condensate	25	2.5	nd	0.2 ng					40
I-8	Impinger	100	4.0							0
I-9	Cyclone	27	3.0	0.2 ng	0.66 ng	.90	0.1 ng	0.07 ng	.86	55
I-10	Cyclone	26	3.0	0.8 ng	0.1 ng	.80	0.9 ng	0.1 ng	.74	60
No. 3[3]	Blank	100	3.0	nd	<.08 ng					10
I-11	Cyclone	26	3.0	0.3 ng	0.1 ng	.78	0.3 ng	0.1 ng	.81	60

(continued)

ANALYSIS OF COMBUSTION RELATED SAMPLES FOR 2,3,7,8-TCDD AND CO-ELUTING AND PRE-ELUTING ISOMERS BY GAS LIQUID CHROMATOGRAPHY/HIGH RESOLUTION MASS SPECTROMETRY (continued)

Analytical sample no.	Nature of sample	Sample wt. or percent analyzed	Ng spike added	2,3,7,8-TCDD and Co-eluters			Pre-eluters			Percent recovery
				Conc. (ppb)[1] or amount (ng)	Detection limit	Isotope[2] ratio	Conc. (ppb)[1] or amount (ng)	Detection limit	Isotope[2] ratio	
I-12	Particle filter	100	3.0 ng	nd	0.06 ng					65
I-13	Probe rinse	26	3.0	0.2 ng 0.1 ng	0.04 ng 0.05 ng	.89	nd nd	0.09 ng 0.06 ng		75
I-14	XAD-resin	11.28 g	3.0	0.37 ppb	0.02 ppb	.76	0.57 ppb	0.02 ppb	.75	25
I-15	Condensate	25	3.0	6.3 ng	0.4 ng	.79	4.6 ng	0.3 ng	.74	30
I-16	Impinger	100	4.0							0
No. 4[3]	Blank	100	3.0	nd	<.02 ng					45

FOOTNOTES:

1. Either concentration in part-per-billion (ppb) or amount of TCDD in nanograms (ng) in the total sample.

2. Typical values are .77 ± .10; however, deviation by ± .15 is not unusual when low levels and/or complicated sample types are encountered.

3. Solvent Blank - assume 100 percent of sample analyzed.

Table 1A.

Analysis of TCDD in Combustion Related Samples by Gas Liquid Chromatography/High Resolution Mass Spectrometry
(Reported as pgs/total sample)

Analytical Sample Number	Nature of Sample	ngs Spike	2,3,7,8 & Coeluters		Preeluters		% Recovery
			pgs/sample	Detection Limit(pgs)	pgs/sample	Detection Limit(pgs)	
1	filter	2.25	190	70	510	120	60
2	resin	2.33	2400	230	8400	280	30
3	impinger	2.25	nd	30	nd	45	60
4	filter	2.25	nd	90	nd	90	95
5	resin	2.25	1800	180	4900	230	40
6	filter	2.25	nd	40	nd	50	70
7	resin	2.25	nd	85	nd	110	65
8	filter	2.25	980	85	7000	110	70
9	resin	2.33	nd	90	nd	85	65
10	resin	2.33	nd	100	nd	100	55
11	filter	2.18	9100	580	1800	580	45[1]
12	resin	2.25	13000	640	12000	250	35[1,3]
13	impinger	2.40	110	70	nd	90	55
14	resin	2.40	nd	55	nd	80	65
15	filter	2.25	nd	55	nd	80	60
16	filter	2.18	nd	290	nd	480	50[2]
17	filter	2.25	1300	190	4000	390	35[3]
18	resin	2.40	13000	380	28000	380	35[1]
19	resin	2.25	nd	80	nd	80	60
20	impinger	2.29	nd	40	nd	50	75
21	filter	2.25	nd	390	nd	590	65[2]
22	resin	2.25	11000	340	15000	340	75

Analytical Sample Number	Nature of Sample	ngs Spike	2,3,7,8 & Coeluters		Preeluters		% Recovery
			pgs/sample	Detection Limit(pgs)	pgs/sample	Detection Limit(pgs)	
23	filter	2.25	2330	250	2700	250	30
24	resin	2.25	nd	90	nd	110	55
25	filter	2.33	nd	190	nd	400	55[2]
26	resin	2.25	nd	190	nd	140	40
27	impinger	2.25	nd	20	----	----	75[7]
28	filter	2.25	2100	310	3200	420	65
29	resin	2.25	nd	70	nd	65	90
30	impinger	2.25	nd	45	----	----	25[7]
31	filter	2.25	460	50	700	65	70
32	resin	2.25	118000	1300	249000	2700	40[5]
33	impinger	2.18	1300[4]	70	4400	140	50
34	resin	2.25	170	100	320	100	20
35	impinger	2.25	290	40	990	35	35
36	filter	2.25	nd	200	nd	290	85
37	filter	2.25	nd	150	----	----	35[7]
38	filter	2.25	370	40	650	90	75
39	resin	2.25	98000	3000	240000	3200	--[6]
40	resin	2.25	nd	140	240	150	15
41	filter	2.25	nd	110	nd	120	80

Analytical Sample Number	Nature of Sample	ngs Spike	2,3,7,8 & Coeluters		Preeluters		% Recovery
			pgs/sample	Detection Limit(pgs)	pgs/sample	Detection Limit(pgs)	
Blank 1	Soxhlet	2.25	nd	20	nd	55	25
Blank 2	Soxhlet	2.25	nd	70	nd	60	35
Blank 3	Distillation Column	2.25	nd	50	nd	55	70
Blank 4	Soxhlet	2.25	nd	40	nd	55	40
Blank 5	Soxhlet	2.25	nd	80	nd	85	65
Blank 6	Soxhlet	2.25	nd	150	nd	230	30
Blank 7	Soxhlet	2.25	nd	30	--	--	35
Blank 8	Soxhlet	2.25	17	16	26	17	45

Footnotes:

1. interference observed at m/z 334
2. interference observed at m/z 322
3. many additional isomers observed
4. average of 2 determinations; 1200, 1400
5. estimated - based on internal standard signal which is partially resolved from a larger interfering signal
6. The internal standard was significantly unresolved from an interfering signal at m/z 334. Therefore, a typical recovery of 50% was assumed. This assumed recovery is based on previous experience and the mean for samples in this report (53 ± 20%). Further, the unresolved signal does indeed correspond to 50% recovery.
7. Signals for preeluters were not recorded for these samples, however, no preeluting TCDD was visually observed with detection limits estimated to be 100pgs.

Table 1B.

Analysis of TCDF in Combustion Related Samples by Gas Liquid Chromatography/High Resolution Mass Spectrometry
(Reported in pgs/total sample)

		2,3,7,8 & Coeluters			Preeluters		
Analytical Sample Number	Nature of Sample	pgs/sample	Detection Limit(pgs)	Ratio[7]	pgs/sample	Detection Limit(pgs)	Ratio[7]
1	filter	3900	220	0.77	6100	330	0.76
2	resin	20000	1300	0.79	40000	1600	0.80
3	impinger	420	220	0.82	650	230	0.69[2]
4	filter	350	180	0.72	370	100	0.69
5	resin	50000	1800	0.78	38000	890	0.76
6	filter	nd	210	----	nd	190	----
7	resin	320000[8]	2700	0.78	1500	170	0.78
8	filter	nd	390	----	nd	430	----
9	resin	460	310	0.75	nd	660	1.35[3]
10	resin	nd	260	----	nd	250	1.38[3]
11	filter	60000	1200	0.76	65000	1200	0.77
12	resin	134000	2700	0.79	126000	2700	0.75
13	impinger	500	180	0.76	740	210	0.71
14	resin	nd	140	----	nd	250	----
15	filter	200	60	0.69	nd	40	----
16	filter	1200	700	0.76	940	400	0.78
17	filter	15000	1400	0.76	16000	1400	0.82
18	resin	8600	490	0.79	15000	960	0.82
19	resin	nd	110	----	nd	140	----
20	impinger	nd	45	----	nd	55	----
21	filter	1000	340	0.81	1100	320	0.71[1]
22	resin	51000	2000	0.79	61000	2000	0.77

Analytical Sample Number	Nature of Sample	2,3,7,8 & Coeluters			Preeluters		
		pgs/sample	Detection Limit(pgs)	Ratio	pgs/sample	Detection Limit (pgs)	Ratio
23	filter	9600	2200	0.88	14000	2700	0.82
24	resin	nd	55	----	nd	120	0.66[6]
25	filter	nd	450	0.93[3]	nd	750	1.00[2,3]
26	resin	nd	95	----	nd	90	----
27	impinger	nd	25	----	nd	25	----
28	filter	nd	140	----	nd	240	----
29	resin	nd[5]	60	----	nd[5]	40	----
30	impinger	nd[5]	110	----	nd	130	----
31	filter	4400	460	0.80	5700	600	0.69
32	resin	1420000	24000	0.81	2250000	50000	0.76
33	impinger	10000	400	0.76	224000	800	0.79
34	resin	nd	160	----	nd	185	----
35	impinger	2300	250	0.81	2300	250	0.81
36	filter	nd[5]	110	----	350	140	0.72
37	filter	nd	65	----	nd	85	----
38	filter	1700	160	0.83	2300	180	0.75
39	resin	980000	19000	0.79	1860000	40000	0.76
40	resin	nd	250	----	nd	310	----
41	filter	nd	40	----	nd	70	----

Analytical Sample Number	Nature of Sample	2,3,7,8 & Coeluters			Preeluters		
		pgs/sample	Detection Limit(pgs)	Ratio	pgs/sample	Detection Limit (pgs)	Ratio
Blank 1	Soxhlet	nd	140	----	nd	160	----
Blank 2	Soxhlet	nd	75	----	nd	75	----
Blank 3	Distillation Column	300[4]	140	0.79	nd	135	----
Blank 4	Soxhlet	240[4]	120	0.72	nd	120	----
Blank 5	Soxhlet	nd	50	----	nd	50	----
Blank 6	Soxhlet	nd	900	----	nd	2000	----
Blank 7	Soxhlet	nd	150	----	nd	180	----
Blank 8	Soxhlet	nd	80	----	nd	110	----

Footnotes:

1. Additional overlapping peaks make quantitation in this sample approximate.
2. Many signals in each mass region may mask lower levels of TCDF.
3. Signals are observed at m/z 320 and 322. However, the isotope ratio is wrong and these samples are thus considered "not detected".
4. These samples were run immediately after SAS 7, which was still tailing low levels of TCDF, and probably does not indicate contamination in the sample extraction procedure.
5. Weak signal below detection limit of 2.5 X noise level.
6. Ratio incorrect, therefore not detected. The signal is observed just at the detection limit.
7. Isotope ratio for m/z 320/322 - acceptable values are 0.77 ± 0.10.
8. 320000 ± 80000

Table 2. Analysis of Total TCDD and TCDF in Combustion Related Samples by GC/HRMS

Analytical Sample Number NLR-10/23-80-1900 GS/HB -	Nature of Sample	Weight Used	Ngs Spiked	Total TCDD Concentration pg/sample		Detection Limit		Total TCDF Concentration pg/sample		Detection Limit		Percent Recovery
				pre	co	pre	co	pre	co	pre	co	
-2I,1,2,3	Impinger	all	9.3	690	360	80	45	4600	5900	190	380	100+
-2CD	Condensate	all	9.4	3200	1100	150	100	46300	25800	830	410	90
-2XR	Resin	all	9.6	21100	4300	1300	1200	184000	99400	1500	740	50
-2PR	Probe	all	9.4	nd	nd	100	160	nd	570	200	200	40
-2PF	Particle filter	all	8.9	180	400	150	260	1500	1000	120	85	50
-2-IC	Cyclone	all	9.3	100	130	85	80	420	510	35	30	50
-2-3C	Cyclone	all	9.4	450	200	190	160	230	900	10	95	60
-2-10C	Cyclone	all	9.3	nd	400	40	270	2400	2200	210	210	15
ESP ASH A(1)	Fly Ash (A)	10g	8.8	400 ppt	200 ppt	18 ppt	35 ppt	8000 ppt	4300 ppt	260 ppt	130 ppt	40
ESP ASH B(1)	Fly Ash (B)	10g	9.0	5300 ppt	2000 ppt	140 ppt	70 ppt	111400 ppt	42700 ppt	750 ppt	750 ppt	50
XAD Resin	XAD Resin	32g	9.2	nd	nd	640	680	2000	1500	400	400	60
	Blank (1)	10g	8.9	nd	nd	10 ppt	10 ppt	nd	nd	15 ppt	15 ppt	40
	Blank (2)	10g	9.0	nd	nd	2 ppt	2 ppt	nd	nd	10 ppt	10 ppt	80

ppt = parts-per-trillion   Ngs = Nanograms   pg = picogram

Table 3. Retention Times of the TCDD Isomers

				Retention Time (RT) in Minutes							
Chemical Analogue (CA)	RT of CA	Isomer No.	D / D/16	SAS 2	SAS 5	SAS 11	SAS 12	SAS 22	SAS 31	SAS 32	SAS 39
		D/01	0.945								35.33
1,3,6,8-TCDD	35.43	D/02	0.948	35.48			35.43	35.47			
		D/03	0.950		35.55				35.50	35.52	
		D/04	0.953				35.67				35.60
		D/05	0.956	35.75	35.78	35.77		35.72	35.73	35.77	
		D/06	0.961	35.97			35.93		35.97		35.88
		D/07	0.964		36.05	36.05		36.00		36.05	
		D/08	0.974				36.42				36.42
		D/09	0.977	36.53	36.57	36.57	36.58	36.52	36.50	36.55	36.52
		D/10	0.980	36.62	36.65	36.68	36.68	36.62	36.62	36.70	36.67
		D/11	0.984	36.78	37.80	36.82	36.77	36.80	37.75	36.82	
		D/12	0.990		37.03		36.96	37.03	37.03		36.93
		D/13	0.992	37.07	37.08	37.07				37.08	37.10
1,2,3,4-TCDD	37.22	D/14	0.996				37.22				37.25
		D/15	0.998	37.28	37.32	37.33	37.30	37.28	37.27	37.32	
2,3,7,8-TCDD	37.38	D/16	1.000	37.38	37.38	37.43	37.37	37.38	37.38	37.40	37.38
		D/17	1.005		37.55		37.50	37.55		37.60	37.58
		D/18	1.007			37.62	37.68				
		D/19	1.011	37.78	37.77	37.82		37.75		37.82	
		D/20	1.016		37.98	38.03	37.92			38.03	
		D/21	1.028		38.28	38.35	38.27			38.33	

D/D16 = Retention time relative to 2,3,7,8-TCDD

Table 4. Percentage Distribution of TCDD Isomers

	Percent Estimated by the Peak Height of m/z 322							
Isomer No.	SAS #2	SAS #5	SAS #11	SAS #12	SAS #22	SAS #31	SAS #32	SAS #39
D/01								11.9
D/02	3.6			0.9	2.7			
D/03		1.9				10.7	2.3	
D/04				5.4				16.5
D/05	12.2	6.5	9.8		21.4	18.0	15.7	
D/06	10.2			3.8		5.7		6.8
D/07		2.8	2.7		7.0		5.3	
D/08				5.7				15.5
D/09	16.5	7.5	8.1	12.1	12.4	16.0	17.8	10.3
D/10	8.8	10.8	9.2	5.4	7.5	6.7	9.3	7.7
D/11	10.4	7.3	7.9	4.1	7.2	7.4	8.9	
D/12		9.1		7.6	6.2	6.5		3.6
D/13	7.2	7.6	8.3			5.7		10.5
D/14				16.9				10.0
D/15	11.1	9.0	21.6	12.5	13.9	16.0	11.3	
D/16	13.8	16.5	14.9	8.9	12.9	12.6	10.6	3.6
D/17		7.2		6.0	5.5		6.0	2.7
D/18			9.4	4.4				
D/19	5.8	6.9	2.3		2.8		4.2	
D/20		3.3	2.7	2.8			1.1	
D/21		3.5	2.5	2.5			1.1	

Table 5.

SAS #2 TCDD

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 322	Weight in picograms
D/02	35.48	3.6	390
D/05	35.75	12.2	1320
D/06	35.97	10.2	1100
D/09	36.53	16.5	1780
D/10	36.62	8.8	950
D/11	36.78	10.4	1120
D/13	37.07	7.2	780
D/15	37.28	11.1	1200
D/16	37.38	13.8	1490
D/19	37.78	5.8	630

Detection Limit 180pg

Total TCDD 10760pg

Table 6.

SAS #5 TCDD

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 322	Weight in picograms
D/03	35.55	1.9	130
D/05	35.78	6.5	435
D/07	36.05	2.8	190
D/09	36.57	7.5	500
D/10	36.65	10.8	720
D/11	37.80	7.3	490
D/12	37.03	9.1	610
D/13	37.08	7.6	510
D/15	37.32	9.0	600
D/16	37.38	16.5	1105
D/17	37.55	7.2	480
D/19	37.77	6.9	460
D/20	37.98	3.3	220
D/21	38.28	3.5	235

Detection Limit 45pg
Total TCDD 6685pg

Table 7.

SAS #11 TCDD

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 322	Weight in picograms
D/05	35.77	9.8	2660
D/07	36.05	2.7	730
D/09	36.57	8.1	2195
D/10	36.68	9.2	2490
D/11	36.82	7.9	2140
D/13	37.07	8.3	2250
D/15	37.33	21.6	5850
D/16	37.43	14.9	4040
D/18	37.62	9.4	2550
D/19	37.82	2.3	620
D/20	38.03	2.7	730
D/21	38.35	2.5	680

Detection Limit 430pg

Total TCDD 26935pg

Table 8.

SAS #12 TCDD

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 322	Weight in picograms
D/02	35.43	0.9	260
D/04	35.67	5.4	1460
D/06	35.93	3.8	1030
D/08	36.42	5.7	1540
D/09	36.58	12.1	3270
D/10	36.68	5.4	1460
D/11	36.77	4.1	1110
D/12	36.96	7.6	2050
D/14	37.22	16.9	4560
D/15	37.30	12.5	3375
D/16	37.37	8.9	2400
D/17	37.50	6.0	1620
D/18	37.68	4.4	1190
D/20	37.92	2.8	755
D/21	38.27	2.5	675

Detection Limit 215pg

Total TCDD 26755pg

Table 9.

SAS #22 TCDD

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 322	Weight in picograms
D/02	35.47	2.7	700
D/05	35.72	21.4	5560
D/07	36.00	7.0	1820
D/09	36.52	12.4	3220
D/10	36.62	7.5	1950
D/11	36.80	7.2	1870
D/12	37.03	6.2	1610
D/15	37.28	13.9	3610
D/16	37.58	12.9	3350
D/17	37.55	5.5	1430
D/19	37.75	2.8	730

Detection Limit 220pg

Total TCDD 25850pg

Table 10.

SAS #31 TCDD

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 322	Weight in picograms
D/03	35.50	10.7	125
D/05	35.73	18.0	210
D/06	35.97	5.7	70
D/09	36.50	16.0	185
D/10	36.62	6.7	80
D/11	37.75	7.4	860
D/12	37.03	6.5	75
D/15	37.27	16.0	185
D/16	37.38	12.6	150

Detection Limit 5 pg

Total TCDD 1940pg

Table 11.

SAS #32 TCDD

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 322	Weight in picograms
D/03	35.52	2.3	3290
D/05	35.77	15.7	22440
D/07	36.05	5.3	7570
D/09	36.55	17.8	25440
D/10	36.70	9.3	13290
D/11	36.82	8.9	12720
D/13	37.08	5.7	8150
D/15	37.32	11.3	16150
D/16	37.40	10.6	15150
D/17	37.60	6.0	8580
D/19	37.82	4.2	6000
D/20	38.03	1.1	1570
D/21	38.33	1.1	1570

Detection Limit 85 pg

Total TCDD 141,920pg

Table 12.

SAS #39 TCDD

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 322	Weight in picograms
D/01	35.33	11.9	19990
D/04	35.60	16.5	27720
D/06	35.88	6.8	11420
D/08	36.42	15.5	26040
D/09	36.52	10.3	17300
D/10	36.67	7.7	12940
D/12	36.93	3.6	6050
D/13	37.10	10.5	17640
D/14	37.25	10.0	16800
D/16	37.38	3.6	6050
D/17	37.58	2.7	4540

Detection Limit 1925pg

Total TCDD 166,490pg

Table 13. Retention Time of the TCDF Isomers

Chemical Analogue(C.A.)	R.T of C.A.	Isomer No.	F/F17	Retention Time (RT) in Minutes								
				SAS 2	SAS 5	SAS 7	SAS 11	SAS 12	SAS 22	SAS 31	SAS 32	SAS 39
		F/01	0.928									25.45
		F/02	0.938								25.73	25.70
		F/03	0.942				25.83		25.80		25.85	25.83
		F/04	0.945	25.90	25.93		25.95	25.90	25.93		25.95	25.90
		F/05	0.948	26.00			26.03					25.98
		F/06	0.950	26.05								26.08
		F/07	0.955	26.20			26.20			26.15	26.15	
		F/08	0.961							26.38	26.33	26.33
		F/09	0.965	26.47			26.47		26.43		26.50	26.48
		F/10	0.969		26.58			26.57	26.57	26.52		
		F/11	0.972	26.62			26.60	26.67	26.68	26.65	26.63	26.63
		F/12	0.975	26.75	26.73		26.73				26.73	26.77
		F/13	0.980	26.90	26.88		26.87	26.83	26.87	26.82		
		F/14	0.984							27.00	26.97	26.98
		F/15	0.987	27.10	27.08		27.08	27.05	27.07			
		F/16	0.993	27.27	27.28		27.27	27.23	27.27	27.18	27.18	27.18
2,3,7,8-TCDF	27.40	F/17	1.000	27.43	27.43	27.37	27.43	27.40	27.38	27.37	27.37	27.38
		F/18	1.009							27.70	27.70	27.67
		F/19	1.012	27.80	27.77		27.77	27.75	27.95			
		F/20	1.017	27.93	27.93		27.90	27.90	27.88	27.83	27.83	27.83

F/F17 - Retention time relative to 2,3,7,8-TCDF

Table 14. Percentage Distribution of TCDF Isomers

	Percent Estimated by the Peak Height of m/z 306							
Isomer No.	SAS #2	SAS #5	SAS #11	SAS #12	SAS #22	SAS #31	SAS #32	SAS #39
F/01								1.1
F/02							2.9	2.3
F/03			2.7		3.5		4.8	8.0
F/04	4.8	7.6	1.9	3.3	3.3		3.6	6.1
F/05	9.3		1.5					3.2
F/06	4.3							5.9
F/07	3.9		0.9			6.4	2.8	
F/08						9.6	5.2	7.7
F/09	8.3		2.1		2.6		5.1	3.3
F/10		4.4		4.8	4.6	7.6		
F/11	3.9		3.7	6.4	10.5	5.7	7.3	4.9
F/12	9.8	4.6	2.9				18.4	20.9
F/13	14.1	14.7	25.8	27.1	24.4	18.5		
F/14						8.3	7.3	6.1
F/15	7.9	7.6	9.4	7.5	5.3			
F/16	4.3		9.0	5.9	4.9	5.1	8.8	8.4
F/17	16.3	29.6	24.4	28.6	26.7	21.7	20.2	10.7
F/18						8.3	9.0	6.9
F/19	6.6	9.5	7.2	8.8	7.1			
F/20	5.8	9.9	8.6	7.2	6.5	8.3	3.9	4.5

Table 15.

SAS #2 TCDF

Isomer NO.	Retention Time in Minutes	% Estimated by the peak height of m/z 306	Weight in picograms
F/04	25.90	4.8	2880
F/05	26.00	9.3	5580
F/06	26.05	4.3	2580
F/07	26.20	3.9	2340
F/09	26.47	8.3	4980
F/11	26.62	3.9	2340
F/12	26.75	9.8	5880
F/13	26.90	14.1	8460
F/15	27.10	7.9	4740
F/16	27.27	4.3	2580
F/17	27.43	16.3	9720
F/19	27.80	6.6	3960
F/20	27.93	5.8	3480

Detection Limit 95pg

Total TCDF 59,520pg

Table 16.

SAS #5 TCDF

Isomer NO.	Retention Time in Minutes	% Estimated by the peak height of m/z 306	Weight in picograms
F/04	25.93	7.6	6690
F/10	26.58	4.4	3870
F/12	26.73	4.6	4050
F/13	26.88	14.7	12940
F/15	27.08	7.6	6690
F/16	27.28	4.2	3695
F/17	27.43	29.6	26050
F/19	27.77	9.5	8360
F/20	27.93	9.9	8710

Detection Limit 100pg

Total TCDF 81,055pg

Table 17.

SAS #11 TCDF

Isomer NO.	Retention Time in Minutes	% Estimated by the peak height of m/z 306	Weight in picograms
F/03	25.83	2.7	3375
F/04	25.95	1.9	2375
F/05	26.03	1.5	1875
F/07	26.20	0.9	1125
F/09	26.47	2.1	2625
F/11	26.60	3.7	4625
F/12	26.73	2.9	3625
F/13	26.87	25.8	32250
F/15	27.08	9.4	11750
F/16	27.27	9.0	11250
F/17	27.43	24.4	30500
F/19	27.77	7.2	9000
F/20	27.90	8.6	10750

Detection Limit 150pg

Total TCDF 125,125pg

Table 18.

SAS #12 TCDF

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 306	Weight in picograms
F/04	25.90	3.3	8580
F/10	26.57	4.8	12480
F/11	26.67	6.4	16640
F/13	26.83	27.1	70460
F/15	27.05	7.5	19500
F/16	27.23	5.9	15340
F/17	27.40	28.6	74360
F/19	27.75	8.8	22880
F/20	27.90	7.2	18720

Detection Limit 2990pg

Total TCDF 258,960pg

Table 19.

SAS #22 TCDF

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 306	Weight in picograms
F/03	25.80	3.5	3920
F/04	25.93	3.3	3690
F/09	26.43	2.6	2910
F/10	26.57	4.6	5150
F/11	26.68	10.5	11760
F/13	26.87	24.4	27320
F/15	27.07	5.3	5930
F/16	27.27	4.9	5480
F/17	27.38	26.7	29900
F/19	27.95	7.1	7950
F/20	27.88	6.5	7280

Detection Limit 1485pg

Total TCDF 111,290pg

Table 20.

SAS #31 TCDF

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 306	Weight in picograms
F/07	26.15	6.4	650
F/08	26.38	9.6	970
F/10	26.52	7.6	770
F/11	26.65	5.7	575
F/13	26.82	18.5	1870
F/14	27.00	8.3	840
F/16	27.18	5.1	515
F/17	27.37	21.7	2190
F/18	27.70	8.3	840
F/20	27.83	8.3	840

Detection Limit 480pg

Total TCDF 10,060pg

Table 21.

SAS #32 TCDF

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 306	Weight in picograms
F/02	25.73	2.9	106430
F/03	25.85	4.8	176160
F/04	25.95	3.6	132120
F/07	26.15	2.8	102760
F/08	26.33	5.2	190840
F/09	26.50	5.1	187170
F/11	26.63	7.3	267910
F/12	26.73	18.4	675280
F/14	26.97	7.3	267910
F/16	27.18	8.8	322960
F/17	27.37	20.2	741340
F/18	27.70	9.0	330300
F/20	27.83	3.9	143130

Detection Limit 16515pg

Total TCDF 3,644.310pg

Table 22.

SAS #39 TCDF

Isomer No.	Retention Time in Minutes	% Estimated by the peak height of m/z 306	Weight in picograms
F/01	25.45	1.1	15600
F/02	25.70	2.3	32620
F/03	25.83	8.0	113460
F/04	25.90	6.1	86510
F/05	25.98	3.2	45380
F/06	26.08	5.9	83675
F/08	26.33	7.7	109200
F/09	26.48	3.3	46800
F/11	26.63	4.9	69490
F/12	26.77	20.9	296410
F/14	26.98	6.1	86510
F/16	27.18	8.4	119130
F/17	27.38	10.7	151750
F/18	27.67	6.9	97860
F/20	27.83	4.5	63820

Detection Limit 5320pg

Total TCDF 1,418.215pg

Table 23. Retention Times of the TCDD Isomers

Chemical Analogue (C. A.)	Retention Time of C.A.	Isomer No.	D/D16	Retention Time (R.T.) in Minutes NLR-10/23/80 - 1900 GS/HB -- -2CD	-2XR
		D/01	0.945	34.83	34.87
		D/04	0.952	35.10	35.13
		D/06	0.960	35.37	35.40
		D/07	0.964	35.53	35.58
		D/08	0.974	35.90	35.93
		D/09	0.979	36.00	36.03
		D/10	0.980	36.13	36.17
		D/12	0.988	36.40	36.43
1,2,3,4-TCDD	36.67	D/14	0.995	36.67	36.68
		D/15	0.997	36.75	36.77
2,3,7,8-TCDD	36.88	D/16	1.000	----	----
			1.002	36.95	36.93
		D/18	1.007	37.12	37.17
		D/20	1.015		37.38

D/D16 - Retention time relative to 2,3,7,8-TCDD

Table 24. Percentage Distribution of TCDD Isomers

Percent Estimated by the Peak Height of m/z 322

Isomer No.	NLR-10/23/80 1900 GS/HB - 2CD	NLR-10/23/80 1900 GS/HB-2XR
D/01	22.6	20.1
D/04	8.2	12.5
D/06	12.2	8.0
D/07	4.2	3.6
D/08	11.9	14.5
D/09	5.9	7.5
D/10	5.7	10.1
D/12	5.4	4.0
D/14	9.9	6.1
D/15	6.5	7.1
	3.9	2.2
D/18	3.4	2.8
D/20		1.4

Table 25.

NLR - 10/23/80 - 1900 GS/HB-2CD

Isomer No.	Retention Time in Minutes	Percent Estimated by the Peak Height of m/z 322	Weight in Picograms
D/01	34.83	22.6	1290
D/04	35.10	8.2	470
D/06	35.40	12.2	695
D/07	35.53	4.2	240
D/08	35.90	11.9	680
D/09	36.00	5.9	335
D/10	36.13	5.7	325
D/12	36.40	5.4	305
D/14	36.67	9.9	565
D/15	36.75	6.5	370
	36.95	3.9	220
D/18	37.12	3.4	190

Total TCDD - 5685 picograms

Detection Limit-120 picograms

Table 26.

NLR - 10/23/80 - 1900 GS/HB-2XR

Isomer No.	Retention Time in Minutes	Percent Estimated by the Peak Height of m/z 312	Weight in Picograms
D/01	34.87	20.1	5970
D/04	35.13	12.5	3710
D/06	35.40	8.0	2375
D/07	35.58	3.6	1070
D/08	35.93	14.5	4305
D/09	36.03	7.5	2225
D/10	36.17	10.1	3000
D/12	36.43	4.0	1190
D/14	36.68	6.1	1810
D/15	36.77	7.1	2110
	36.93	2.2	655
D/18	37.17	2.8	830
D/20	37.42	1.4	415

Total TCDD - 29665 picograms

Detection Limit - 240 picograms

Table 27. Retention Times of the TCDF Isomers

Chemical Analogue (C.A.)	Retention Time of C.A.	Isomer No.	F/F17	Retention Times (R.T.) in Minutes NLR - 10/23/80 - 1900 GS/HB -- -2CD	 -2XR	 -2PF + -2 -1C
			0.916	24.38	24.40	
		F/01	0.929	24.75	24.77	
		F/02	0.939	25.00	25.03	
		F/03	0.943	25.10	25.13	
		F/05	0.948	25.27	25.23	
		F/06	0.952	25.37	25.35	
		F/07	0.954		25.42	
		F/08	0.961	25.60		
		F/09	0.964	25.67	25.67	
		F/10	0.968	25.78	25.82	
		F/11	0.972	25.90		
		F/12	0.975	25.98	25.95	
		F/13	0.979	26.07	26.08	26.08
		F/15	0.987	26.27	26.30	
			0.991	26.38	26.40	
		F/16	0.993	26.45	26.47	
2,3,7,8-TCDF	26.64	F/17	1.000	26.63	26.65	26.65
		F/19	1.013	26.97	27.00	
		F/20	1.018	27.12	27.13	

F/F17 - Retention time relative to 2,3,7,8-TCDF

Table 28. Percentage Distribution of TCDF Isomers

Percent Estimated by the Peak Height of m/z 306

Isomer No.	NLR - 10/23/80 1900 GS/HB - 2CD	NLR - 10/23/80 1900 GS/HB - 2XR
F/01	2.0	2.8
F/02	2.3	3.2
F/03	9.2	12.1
F/05	3.9	4.9
F/06	4.5	3.8
F/07		6.9
F/08	9.5	
F/09	3.0	6.7
F/10	2.6	4.4
F/11	7.1	
F/12	4.8	5.3
F/13	14.1	15.7
F/15	4.4	3.1
	2.2	2.1
F/16	3.4	3.7
F/17	15.1	14.8
F/19	5.1	3.7
F/20	3.9	4.3

Table 29.

NLR - 10/23/80 - 1900 GS/HB-2CD

Isomer No.	Retention Time in Minutes	Percent Estimated by the Peak Height of m/z 360	Weight in Picograms
	24.38	2.0	1520
F/01	24.75	2.3	1750
F/02	25.00	3.1	2360
F/03	25.10	9.2	7005
F/05	25.27	3.9	2970
F/06	25.37	4.5	3425
F/08	25.60	9.5	7235
F/09	25.67	3.0	2285
F/10	25.78	2.6	1980
F/11	25.90	7.1	5410
F/12	25.98	4.8	3655
F/13	26.07	14.1	10740
F/15	26.27	4.4	3350
	26.38	2.2	1675
F/16	26.45	3.4	2590
F/17	26.63	15.1	11500
F/19	26.97	5.1	3885
F/20	27.12	3.9	2970

Total TCDF - 75975 picograms

Detection Limit - 330 picograms

Table 30

NLR - 10/23/80 - 1900 GS/HB-2XR

Isomer No.	Retention Time in Minutes	Percent Estimated by the Peak Height of m/z 306	Weight in Picograms
	24.40	2.8	5455
F/01	24.77	3.2	6235
F/02	25.03	2.9	5650
F/03	25.13	12.1	23570
F/05	25.23	4.9	9545
F/06	25.35	3.8	7400
F/07	25.42	6.9	13440
F/09	25.67	6.7	13050
F/10	25.82	4.4	8570
F/12	25.95	5.3	10325
F/13	26.08	15.7	30585
F/15	26.30	3.1	6040
	26.40	2.1	4090
F/16	26.47	3.7	7205
F/17	26.65	14.8	28830
F/19	27.00	3.7	7205
F/20	27.13	4.3	8375

Total TCDF - 195570 picograms

Detection Limit -1020 picograms